VOLUME 36 SEPTEMBER 1958 NUMBER 9

Canadian Journal of Chemistry

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CANADIAN JOURNAL OF CHEMISTRY

(*Formerly Section B, Canadian Journal of Research*)

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Canadian Journal of Chemistry

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOLUME 36 SEPTEMBER 1958 NUMBER 9

PEROXIDES IN THE COMBUSTION OF ISOBUTANE[1]

G. W. TAYLOR[2]

ABSTRACT

A survey has been made of the nature of the peroxides occurring in the combustion of isobutane below and above the lower cool-flame limit. The peroxides were resolved and partially identified by paper chromatography. Below the cool-flame limit, the peroxide is found to be mostly *tert*-butyl hydroperoxide, with some hydrogen peroxide, but as the cool-flame limit is approached the proportion of *tert*-butyl hydroperoxide declines, while that of hydrogen peroxide increases. In addition, peroxides identified as aldehyde and acid peroxides increase as the cool-flame limit is approached. No *tert*-butyl hydroperoxide appears to survive the cool flame, although copious quantities of aldehyde peroxide and hydrogen peroxide remain.

INTRODUCTION

The nature and role of the peroxides occurring in the products of the non-catalyzed thermal oxidation of hydrocarbons has been the subject of considerable debate, and the problem has been complicated by the absence of a reliable analytical technique, capable of identifying peroxides in the amounts usually prevailing in the study of combustion reactions. The possible occurrence of various types of peroxides in combustion reactions has recently been considered by Tipper (1). While several unequivocal identifications have been claimed, these are for the most part confined to exceptional cases, for example the low-temperature combustion of acetaldehyde (2).

A paper chromatographic method of resolving some peroxide mixtures has recently been briefly described, and applied in the analysis of the cool-flame combustion products of ethyl benzene (3). The application of this technique has now been extended over a further range of peroxides and its use in the analysis of the combustion products of isobutane is the subject of the present paper.

Isobutane is a rather exceptional fuel, in that it possesses nine primary hydrogen atoms and only one tertiary hydrogen atom. That this latter atom is the initial point of attack by oxygen has been demonstrated by Batten, Gardner, and Ridge (4). Further, the hydroperoxide derived from isobutane, *tert*-butyl hydroperoxide, is unique among the lower alkyl hydroperoxides in its thermal stability. From the point of view of the possible identification of alkyl hydroperoxide in a hydrocarbon oxidation product, the combustion of isobutane thus appears particularly attractive. Batten, Gardner, and Ridge analyzed their combustion products in some detail and, apart from the inevitable gaseous product, found formaldehyde, a smaller amount of higher aldehyde, acetone, a little acid, and peroxides. The peroxides were further examined by polarography with successive removal of various components. Hydrogen peroxide was removed by reaction with

[1]*Manuscript received May 13, 1958.*
Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada.
Issued as N.R.C. No. 4813.
[2]*National Research Council Postdoctorate Fellow 1956–1958.*

titanous chloride and ammonia. Formaldehyde peroxide (and, the authors conclude, higher aldehyde peroxide also) was removed by reaction with mercury. The residual peroxide was assumed on the basis of its polarogram to be alkyl hydroperoxide. From this procedure, the authors concluded that alkyl hydroperoxide, probably *tert*-butyl hydroperoxide, could form more than 50% of the total peroxide.

An examination of their polarograms immediately reveals that the identification of the peroxide is by no means unequivocal, as the authors themselves make clear. Nevertheless, the occurrence of *tert*-butyl hydroperoxide and hydrogen peroxide appeared highly probable, the former compound especially in the induction period.

The present work entirely confirms the conclusions of Batten, Gardner, and Ridge by providing identifications which can be open to very little uncertainty.

EXPERIMENTAL

Isobutane, a gift from the British Petroleum Company Limited, contained 0.5% *n*-butane as the sole detectable impurity. Oxygen was obtained from a cylinder and was used without further treatment.

The reaction was studied using a flow system similar to that already described (3). The reaction vessel was a pyrex cone, 15 cm long, 2.5 cm maximum diameter. The fuel to oxygen ratio was 1 to 1, total pressure atmospheric. The products were passed through a trap at −80° C. At the end of a run the trap was allowed to warm up, isobutane evaporating off. The residual liquid was used in the identification of peroxides. Drops of liquid were paper chromatographed as previously described. The solvent system used was butanol–ether–water (10:10:1). The chromatograms were developed with aqueous acidified potassium iodide solution. The unknown chromatograms were compared with those of standards run on the same paper.

The standard peroxides, whose R_F values are shown in Table I, were: methoxy hydroperoxide and dimethoxyperoxide (formaldehyde peroxides); α-hydroxyethyl hydroperoxide and α,α'-dihydroxydiethyl peroxide (acetaldehyde peroxides); *tert*-butyl hydroperoxide, and hydrogen peroxide. Aldehyde peroxide was made by desiccating an aqueous mixture of aldehyde and hydrogen peroxide containing a drop of sulphuric acid, over concentrated sulphuric acid. The end product of the formaldehyde mixture was a mildly explosive, insoluble solid, shown by Rieche and Meister (5) to be tetraoxymethylene diperoxide. This contained a little material soluble in water, which was dimethoxyperoxide. A compound which was almost certainly methoxy hydroperoxide was obtained only as an intermediate in the initial stage of the reaction. A similar sequence occurred in the acetaldehyde reaction, but here polymer was not obtained. The end product was a hygroscopic, very explosive oil. In addition, butyraldehyde and caproaldehyde were shaken with hydrogen peroxide; some reaction occurred producing compounds of R_F value 0.99–1.0. In general, pure peroxides were not isolated, aqueous solutions being adequate for the present purpose.

RESULTS

The oxidation of isobutane was studied at 250, 330, 360, and 370° C. A cool flame appeared at about 350° C.

(*a*) *At 250° C, total flow 0.4 ml per sec, run time 195 minutes.*—A trace of aqueous product, strongly peroxidic, remained in the trap. The R_F values of the peroxides were 0.99 and 0.50. A smudge, of maximum density at 0.85, also was formed. The component of R_F 0.99 strongly predominated.

(*b*) *At 330° C, total flow 2.0 ml per sec, run time 30 minutes.*—The product was similar to the above. The proportion of material of R_F 0.99 was somewhat decreased, while that of R_F 0.50 increased. The smudge was also denser.

(*c*) *At 360° C, total flow 2.0 ml per sec, run time 15 minutes. Weak cool flame.*—The degree of oxidation was considerably increased, and an appreciable volume of liquid product was formed. The R_F values of the peroxides were 0.50 and 0.9; the latter spot was actually a streak, extending between 0.95 and 0.7. The component of R_F 0.99 was almost certainly absent.

(*d*) *At 370° C, total flow 2.0 ml per sec, run time 30 minutes. Bright cool flame.*—The product was treated as in (*c*). No component of R_F 0.99 was present, although the density of the 0.7–0.95 smudge was considerably increased. The component of R_F 0.50 was also present.

DISCUSSION

A comparison of the R_F values of the unknown peroxides with the R_F values of the standards shows that the unknown peroxide of R_F 0.50 is almost certainly hydrogen peroxide. It is interesting that this compound is a product of the low-temperature reaction, as it has generally been assumed to be characteristic more of a high-temperature reaction. The possibility that the hydrogen peroxide detected is actually a result of decomposition of organic peroxide during the analysis is ruled out by the fact that spots, not streaks, were obtained in the chromatography of the standards.

The spot of R_F 0.99 exactly matches that of *tert*-butyl hydroperoxide. The identification of this component as *tert*-butyl hydroperoxide is strongly substantiated by the conditions of its appearance. It is a product of the induction period, that is, a primary product, and disappears as the degree of reaction increases, that is, as the cool-flame limit is crossed. This behavior is exactly the reverse of that of aldehydes—and hence, aldehyde peroxides—which are the predominant products of cool-flame reactions (e.g. propane (6) and hexane (7)). It is improbable, therefore, that the fast-moving peroxide is a higher aldehyde peroxide possibly derived from the preferential combustion of the trace of *n*-butane in the starting material.

The material of R_F 0.7–0.95 was a minor component below the cool-flame limit, but increased markedly as the limit was crossed. A comparative study of the cool-flame oxidation of a wide variety of hydrocarbons and ethers showed that this material is a characteristic product of all the oxidations. A comparison of its chromatographic behavior with that of the standards suggests that its composition is complex, and it is believed that the material is a mixture of aldehyde and acid peroxides not completely resolved. The presence of alkyl hydroperoxides is not ruled out, but the conditions of its occurrence would appear to preclude the presence of alkyl hydroperoxides.

TABLE I

R_F VALUES OF STANDARD PEROXIDES

Peroxide	R_F
Hydrogen peroxide	0.50
Methoxyhydroperoxide	0.65
Dimethoxyperoxide	0.82
α-Hydroxyethyl hydroperoxide	0.73
α,α'-Dihydroxydiethyl peroxide	0.95
tert-Butyl hydroperoxide	0.99

Solvent: *n*-Butanol–ether–water (10:10:1 v/v).
Paper: Whatman No. 3.
Developer: Acidified potassium iodide.

It is concluded, therefore, that in the oxidation of isobutane, the peroxide products are hydrogen peroxide, *tert*-butyl hydroperoxide, and aldehyde peroxides. *Tert*-butyl hydroperoxide is the predominant product of the induction period, along with some hydrogen peroxide. As the cool-flame limit is passed, the yield of *tert*-butyl hydroperoxide suffers a catastrophic decline while the yields of aldehyde peroxides and hydrogen peroxide increase.

This behavior appears to substantiate the conclusions of Batten, Gardner, and Ridge. The decline in their total peroxide after the induction period was ended (in contrast with the present data) is probably a result of consumption of reactant in their static apparatus.

This work was done while the author was in the Department of Physical Chemistry in the University of Cambridge, England. He is indebted to Prof. R. G. W. Norrish, F.R.S., for inspiration and encouragement.

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THE REACTIONS OF ACTIVE NITROGEN WITH CYCLOPROPANE, CYCLOBUTANE, AND CYCLOPENTANE[1]

N. V. KLASSEN,[2] M. ONYSZCHUK,[3] J. C. MCCABE,[4] AND C. A. WINKLER

ABSTRACT

Cyclopropane, cyclobutane, and cyclopentane in order of increasing reactivity with active nitrogen yielded hydrogen cyanide and ethylene as the major products. The relative proportions of ethylene to hydrogen cyanide increased with number of carbon atoms in the reactant and with increase of temperature.

Alkenes have been found (1) to react with active nitrogen more rapidly than do the corresponding alkanes, to yield a larger proportion of unsaturated hydrocarbons (other than the initial reactant) relative to hydrogen cyanide in the products. It was of interest to determine whether cycloalkanes, in their reactions with active nitrogen, would resemble the corresponding *n*-alkanes or their olefin isomers, and whether the ease of reaction would depend upon the relative stabilities of the cycloalkane rings.

EXPERIMENTAL

The apparatus, experimental techniques, and analytical methods were essentially the same as those described in previous papers (2, 3, 4). A molecular nitrogen flow of 58 micromoles/second at a pressure of 1.5 mm Hg was used in the cyclopropane and cyclobutane reactions, while in the cyclopentane reaction the molecular nitrogen flow was 100 micromoles/second at a pressure of 1.8 mm Hg. In a brief examination of the atomic hydrogen reaction with cyclopentane and ethylene the flow of hydrogen was 120 micromoles/second at a pressure of 0.95 mm Hg.

Cyclopropane of 99.5% purity was used after a single bulb-to-bulb distillation. A limited supply of cyclobutane of approximately 99% purity was obtained through the courtesy of Dr. W. D. Walters, University of Rochester. The cyclopentane used had a refractive index $n_D^{20} = 1.4062$ ($n_D^{20} = 1.4064$ for highly purified cyclopentane (5)). Low temperature fractionation failed to reveal any lower molecular weight impurities.

Analyses for HCN, $(CN)_2$, and NH_3 were made by standard titration methods (6, 7), while mass-spectrometric and gas-chromatographic methods were used for other condensible and the non-condensible products.

RESULTS

Active nitrogen appeared to react only slowly with cyclopropane, since the purple-pink reaction flame completely filled the reaction vessel, even at high reactant flow rates. The flow rate of active nitrogen was taken to be equal to the maximum flow rate of hydrogen cyanide produced in the reaction of ethylene with active nitrogen at temperatures above 250° C (1) and found to be 3.9 micromoles/second.

The recovery of HCN increased as cyclopropane flow rate increased at all temperatures (Fig. 1), hence complete consumption of active nitrogen did not take place except, perhaps, at high flow rates at 350° C. The recoveries of C_2H_4 and C_2H_2 were much smaller than that of HCN (Fig. 1), and C_2H_6 was detected only in trace amounts.

[1]*Manuscript received April 29, 1958.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from Union Carbide of Canada and the National Research Council of Canada.
[2]*Holder of a Union Carbide (Canada) Research Fellowship and a National Research Council Studentship.*
[3]*At the time, holder of a National Research Council Studentship. Now Assistant Professor, McGill University.*
[4]*Present address: Darjeeling Mission, India.*

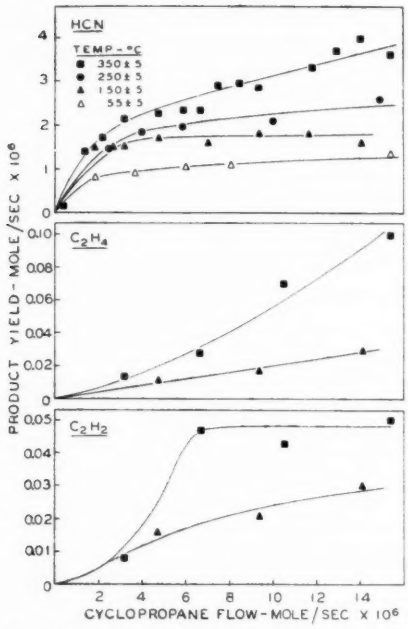

FIG. 1. Relation of cyclopropane flow rate to product yields.

At high flow rates cyclobutane reacted with a relatively intense peach-colored flame in a small volume around the hydrocarbon inlet, from which it might be inferred that cyclobutane was considerably more reactive than cyclopropane. This is confirmed by the much higher conversion to HCN (Fig. 2). Complete reaction of the active nitrogen (the flow rate of which was 5.2 micromoles/second) appeared to be attained only above 250° C and 5 micromoles/second cyclobutane flow, when the production of HCN became independent of reactant flow rate.

The yields of other products in relation to cyclobutane flow rate are also shown in Fig. 2. Propane was detected among the products, but in even smaller amounts than propylene.

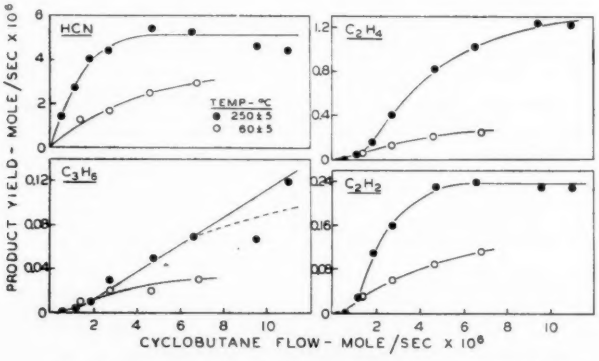

FIG. 2. Relation of cyclobutane flow rate to product yields.

Cyclopentane reacted with active nitrogen with a reddish-violet flame that was concentrated near the hydrocarbon inlet at all but the lowest flow rates, i.e. the reaction appeared to be quite fast. The limiting production of HCN (Fig. 3) was essentially equal to the active nitrogen flow rate of 13 micromoles/second. The largest observed ratio of C_2H_4 to HCN was 0.7, but this ratio would undoubtedly have increased at still higher cyclopentane flow rates (not readily attainable because of back diffusion from the reaction vessel).

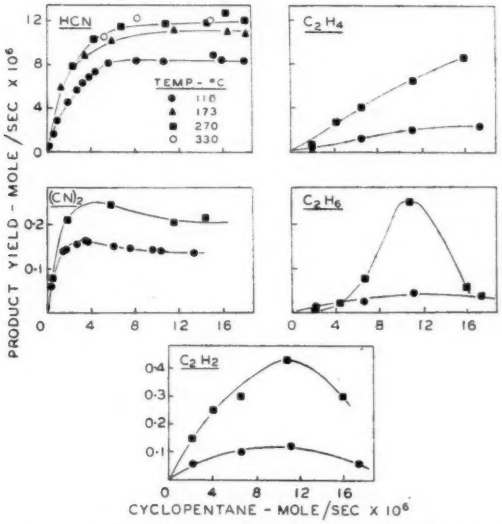

FIG. 3. Relation of cyclopentane flow rate to product yields.

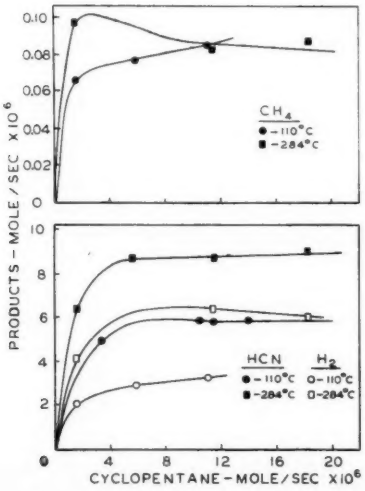

FIG. 4. Relation of cyclopentane flow rate to yields of methane and hydrogen.

The recoveries of $(CN)_2$, C_2H_6, and C_2H_2 showed maxima with cyclopentane flow rate. Ammonia and C_3 and C_4 hydrocarbons were detected in amounts less than 1% of the HCN.

In another series of experiments, with an active nitrogen flow of 9.7 micromoles/sec the productions of CH_4, H_2, and HCN were found to be related to cyclopentane flow, as shown in Fig. 4. Mass-spectrometric and gas-chromatographic analyses indicated that no product in excess of 1% of the HCN remained undetected.

To obtain information about the possible effect of atomic hydrogen on the cyclopentane – active nitrogen reaction, the relative rates of the H atom reactions with cyclopentane and ethylene were examined at 284° C. With the results shown in Table I.

TABLE I

DATA FOR THE REACTIONS OF HYDROGEN ATOMS WITH CYCLOPENTANE AND ETHYLENE AT 284° C

cyclo-C_5H_{10} input	C_2H_4 input	Argon input	C_2H_6 yield	C_2H_4 yield	C_2H_4 destroyed
12.95[a]	—	—	0.170	0.120	—
13.65	—	—	0.170	0.200	—
—	12.65	—	0.920	11.05	1.60
—	13.50	—	1.250	11.95	1.55
—	12.90	11.95	0.920	11.40	1.50
—	13.05	12.00	0.900	11.55	1.50
13.30	12.45	—	0.520	12.10	*ca.* 0.45[b]
13.20	12.85	—	0.420	12.45	*ca.* 0.45[b]

[a]All values refer to flow rates in micromoles/second.

[b]It was assumed that approximately 0.08 micromoles/second of ethylene was produced by reaction of hydrogen atoms with cyclopentane.

Since the hydrocarbon flow (13 micromoles/second) was in large excess over the H atom flow (estimated from the H atom – hydrogen iodide reaction to be about 6 micromoles/second (8)), the reaction of H atoms should have been confined largely to their initial attack on the hydrocarbon. The results obtained with a mixture of ethylene and argon indicate that physical effects in the apparatus used do not invalidate direct comparison between the reactions of hydrocarbon mixtures and the reactions of pure hydrocarbons. Hence, it may be inferred from Table I that ethylene was destroyed three times more slowly when mixed with an equal amount of cyclopentane than when it reacted alone. Therefore, the rates of the reactions of atomic hydrogen with ethylene and cyclopentane are of the same order at 284° C, and any hydrogen atoms produced in the cyclopentane – active nitrogen reaction at 270° C would be expected to react to a large extent with cyclopentane.

TABLE II

KINETIC CONSTANTS FOR THE REACTIONS OF ACTIVE NITROGEN WITH CYCLOALKANES

Cycloparaffin	Temp., °C	k, liter $mole^{-1}sec^{-1} \times 10^{-5}$	E, kcal $mole^{-1}$	P, $\times 10^4$
Cyclopropane	50	0.8	3.2	0.6
	150	2.5		
	250	5.1		
	350	9.1		
Cyclobutane	60	1.2	4.6	4.7
	250	18.		
Cyclopentane	110	2.4	5.3	8.8
	270	19.		

Values of the second-order rate constants for the initial attack of active nitrogen on cyclopropane, cyclobutane, and cyclopentane are shown in Table II. The calculations were made for conditions of incomplete consumption of both cycloalkane and active nitrogen.

DISCUSSION

As in previous papers, it will be assumed that atomic nitrogen is the main chemically reactive species in active nitrogen (9).

It would seem that the reactions of cyclopropane, cyclobutane, and cyclopentane with nitrogen atoms can be explained by similar mechanisms, the initial steps of which are analogous to the primary reaction suggested previously (1) for the reaction of active nitrogen with saturated hydrocarbons, i.e.,

$$\text{cyclo-}C_5H_{10} + N \rightarrow HCN + H_2 + C_4H_7; \quad \Delta H = -10 \text{ to } -40 \text{ kcal.} \qquad [1]$$

$$\text{cyclo-}C_4H_8 + N \rightarrow HCN + H_2 + C_3H_5; \quad \Delta H = -58 \text{ kcal} \qquad [2]$$

$$\text{cyclo-}C_3H_6 + N \rightarrow HCN + H_2 + C_2H_3; \quad \Delta H = -29 \text{ kcal} \qquad [3]$$

An obvious alternative to reaction [1] which would permit a ratio for C_2H_4 to HCN of 0.7, but which would seem to be forbidden by its endothermicity, is the reaction

$$\text{cyclo-}C_5H_{10} + N \rightarrow HCN + 2C_2H_4 + H; \quad \Delta H = +14 \text{ kcal.} \qquad [4]$$

The reaction

$$\text{cyclo-}C_5H_{10} + N \rightarrow HCN + C_2H_4 + C_2H_5; \quad \Delta H = -25 \text{ kcal} \qquad [5]$$

is also a possible alternative to reaction [1]. However, it should be followed by very rapid reaction of C_2H_5, and subsequently CH_3 radicals with active nitrogen to form HCN (1, 10, 11). The attack of nitrogen atoms on cyclopentane almost certainly has a higher activation energy than the radical–nitrogen atom reactions, and more nitrogen atoms should therefore be consumed in the primary step at higher temperatures and cyclopentane flow rates. Consequently, the radicals should suffer correspondingly less destruction and, contrary to the experimental results, the yields of ethane and methane should increase steadily with temperature and cyclopentane flow. Hence it may be concluded that reaction [5] is also of relatively little, if any, importance in the cyclopentane–active nitrogen reaction.

The unsaturated radicals formed in reactions [1], [2], and [3] should be attacked rapidly by nitrogen atoms in reactions such as

$$C_4H_7 + N \rightarrow HCN + C_2H_4 + CH_2 \qquad [6]$$

$$C_3H_5 + N \rightarrow HCN + C_2H_4 \qquad [7]$$

$$C_2H_3 + N \rightarrow HCN + CH_2 \qquad [8]$$

together with the reactions

$$CH_2 + N \rightarrow HCN + H \qquad [9]$$

$$CH_2 + N \rightarrow CN + H_2. \qquad [10]$$

If some of the CH_2 produced in reactions such as [6] or [8] is in the triplet state, the reaction

$$CH_2^* + N \rightarrow CN + 2H \qquad [11]$$

might occur to an appreciable extent.

The large amounts of C_2H_4 formed in the cyclopentane reaction at 270° C can be explained if the previous reactions are accompanied by

$$\text{cyclo-}C_5H_{10} + H \rightarrow \text{cyclo-}C_5H_9 + H_2 \quad [12]$$

and

$$\text{cyclo-}C_5H_{10} + CN \rightarrow \text{cyclo-}C_5H_9 + HCN, \quad [13]$$

followed by

$$\text{cyclo-}C_5H_9 + N \rightarrow HCN + 2C_2H_4. \quad [14]$$

The present study has shown that the attack of cyclopentane by H atoms at 270° C and high cyclopentane flow rates is quite probable even in the presence of considerable ethylene.

The maxima in the production of CH_4 and C_2H_6 from cyclopentane at the higher temperatures may be explained if it is assumed that these arise mainly from CH_3 radicals, and that the radicals are produced as suggested previously (1, 12),

$$C_2H_4 + N \rightarrow HCN + CH_3. \quad [15]$$

The extent of reaction [15] should pass through a maximum with flow rate of cyclopentane, since it is in competition with reaction [1], and this maximum should be more pronounced at higher temperatures, as observed, since the activation energy of reaction [1] (5.3 kcal/mole) appears to be higher than that of reaction [15] (3 kcal/mole (13)). The maximum should be less pronounced for methane than for ethane production, as observed, if methane production resulted mainly from reaction of CH_3 radicals with cyclopentane, while ethane was produced by their recombination.

Recovery of acetylene in small amounts from the three hydrocarbon – N atom reactions may be explained as in an earlier paper (1), i.e. reaction of N atoms with $N \cdot C_2H_4$ complexes to bring about recombination of N atoms and production of triplet ethylene which then decomposes to yield acetylene. Cyanogen probably resulted from the recombination of CN radicals formed in reactions such as [10] and [11].

The large value of the C_2H_4: C_3H_6 ratio in the cyclobutane reaction and the increase of this ratio with temperature indicate that propylene was formed in secondary processes, perhaps by the hydrogenation of C_3H_5 radicals. Similarly, the small quantities of ethylene recovered from the cyclopropane reaction could have resulted from hydrogenation of C_2H_3 radicals, perhaps by abstraction from the parent hydrocarbon.

It is interesting to note that, of the three reactions studied, the cyclopropane reaction appears to have the lowest activation energy. This might be due to greater delocalization of carbon–carbon bond orbitals in cyclopropane (greater *p*-character), thus facilitating the approach of an electrophilic reagent such as a nitrogen atom. A similar situation exists in the ethylene – active nitrogen reaction which also has a low activation energy.

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THE REACTIONS OF ACTIVE NITROGEN WITH CHLOROMETHANES[1]

S. E. Sobering[2] and C. A. Winkler

ABSTRACT

Cyanogen chloride and chlorine were the only gaseous products observed in the reaction of active nitrogen with carbon tetrachloride at 110° and 420° C. The product yields tended towards limiting values at higher reactant flow rates, and increased with increase of temperature at all flow rates. The reactions of active nitrogen with chloroform and dichloromethane at 260° and 420° C yielded hydrogen chloride, hydrogen cyanide, and cyanogen, in addition to cyanogen chloride and chlorine. The behavior of the product yields with reactant flow rates and temperature was similar to that of the products from carbon tetrachloride.

The reactions of active nitrogen with methyl-, ethyl-, propyl-, isopropyl-, and vinyl-chlorides have been discussed in earlier papers from this laboratory (1, 2). The present paper reports the results obtained in a similar study with carbon tetrachloride, chloroform, and dichloromethane, to examine the effect of different extents of halogen substitution.

EXPERIMENTAL

The apparatus and experimental procedures were essentially the same as those used in the previous studies of active nitrogen reactions (3). Standard analytical methods (4, 5, 6) were adapted without serious difficulty to the products of the reactions after they had been given appropriate preliminary separation by low-temperature distillation and chemical absorption (7).

RESULTS AND DISCUSSION

The reaction flames for the three reactions were quite bright, with an orange tint that became progressively less marked with decrease in the number of halogen atoms in the reactant molecule.

A small amount of greenish-brown polymer was formed during each of the reactions. With carbon tetrachloride, but not with the other chloromethanes, a trace of white solid was also deposited. This solid resembled hexachlorethane in its solubility in ether and in its tendency to sublime when heated. Although no chemical analyses of the polymers were made, owing to the difficulty in obtaining sufficient material, they did not behave, when heated, as if they were pure materials such as cyanuric chloride or paracyanogen. Traces of free carbon appeared to be formed in the chloroform and dichloromethane reactions.

With CCl_4, the flow rate of molecular nitrogen was 39 micromoles/second (operating pressure = 1 mm) and that of active nitrogen was estimated to be 9.3 micromoles/second, from the maximum HCN production from ethylene at 425° C (2, 3). The only gaseous products were Cl_2 and CNCl, the yields of which changed with flow rate of CCl_4 in the manner shown in Fig. 1. The ratio of Cl_2 yield to CNCl yield decreased steadily from about 3:1 to a limiting value of 1.5:1 as the flow rate of CCl_4 was increased over the range used.

With $CHCl_3$, a new pumping system was used, and the active nitrogen flow rate was estimated as 14.6 micromoles/second, with a molecular flow of 180 micromoles/second at a pressure of 1.65 mm. The gaseous products were HCl, CNCl, and Cl_2 in comparatively

[1]*Manuscript received April 29, 1958.*
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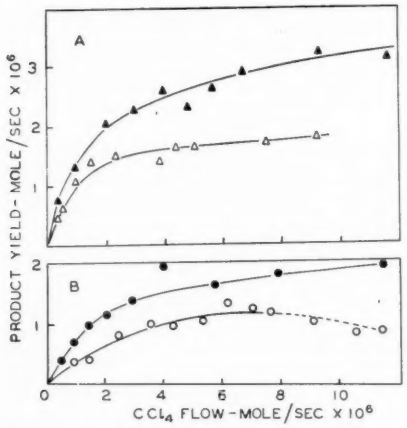

FIG. 1. Relation between carbon tetrachloride flow rate and yields of products.
A = Cl_2 production △ 90° C ▲ 420° C B = CNCl production ○ 90° C ● 420° C

large amounts, together with lesser amounts of HCN and $(CN)_2$. In Fig. 2, which depicts the relations of product yields to $CHCl_3$ flow rates, the total HCN + $(CN)_2$ yields consisted of approximately 40% HCN and 60% $(CN)_2$.

With CH_2Cl_2, the operating conditions were identical with those used for $CHCl_3$. The major products were HCl, HCN, and CNCl, production of which varied with flow rate of CH_2Cl_2 as indicated in Fig. 3. Much smaller quantities of Cl_2 (Fig. 3) and $(CN)_2$ (maximum 0.4 micromoles/second) were produced.

The reactions of active nitrogen with the three chloromethanes of the present study resemble the reaction with methyl chloride studied previously (1) in color and behavior of the reaction flames, in tendency for slight polymer formation, in exothermicity, and in production of HCl and HCN as products when possible. It should be noted that the methyl chloride reaction yielded only HCl and HCN (and hydrogen) as major products; CNCl and Cl_2 were entirely absent.

There seems to be little doubt that the active nitrogen – CCl_4 reaction occurred by

$$N + CCl_4 \rightarrow [N \cdot CCl_4] \rightarrow CNCl + Cl_2 + Cl; \quad \Delta H = -24 \text{ kcal.}$$

The alternative decomposition of the collision complex to yield CN radicals seems unlikely, since no significant quantity of cyanogen was formed.

The observed increase in Cl_2: CNCl ratio with decrease of CCl_4 flow rate suggests that, with excess N atoms, reactions occur of the type

$$N + N \cdot CCl_4 \rightarrow N_2 + CCl_4^*,$$

followed by decomposition of the excited CCl_4 to yield chlorine and perhaps CCl_3, dimerization of which would yield the traces of hexachlorethane that appeared to be formed.

The products from the reaction of chloroform with active nitrogen can be semi-quantitatively explained by the scheme

$$\begin{aligned} N + CHCl_3 \rightarrow [N \cdot CHCl_3] &\rightarrow CNCl + HCl + Cl; \quad \Delta H = -48 \text{ kcal} \\ &\rightarrow HCN + Cl_2 + Cl; \quad \Delta H = -29 \text{ kcal} \\ &\rightarrow CN + HCl + Cl_2; \quad \Delta H = -18 \text{ kcal,} \end{aligned}$$

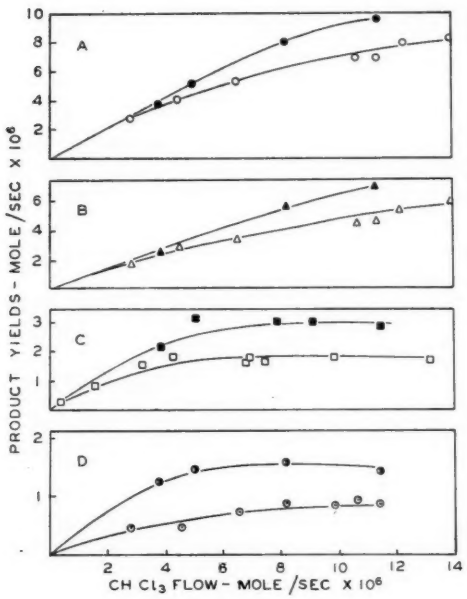

FIG. 2. Relation between chloroform flow rate and yields of products.

A = HCl production ○ 260° C ● 420° C
B = CNCl production △ 260° C ▲ 420° C
C = Cl_2 production □ 260° C ■ 420° C
D = HCN production ⊙ 260° C ◑ 420° C

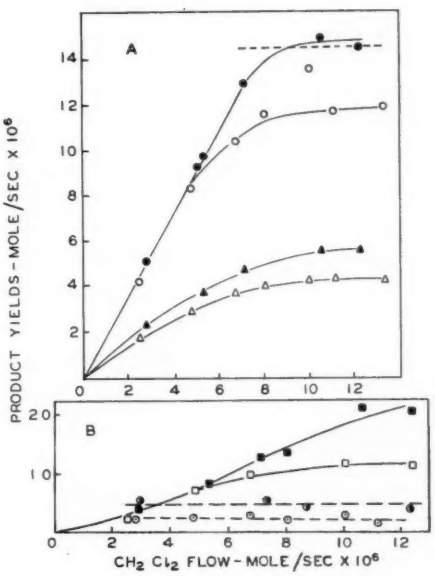

FIG. 3. Relation between dichloromethane flow rate and yields of products.

A = HCl production ○ 255° C ● 425° C
HCN production △ 255° C ▲ 425° C
B = CNCl production □ 255° C ■ 425° C
Cl_2 production ⊙ 255° C ◑ 425° C

Dotted line in panel A represents yield of HCN from ethylene at high temperatures.

in which the first reaction occurs to at least three times the extent of the other two combined. However, compared with the proportions inferred from such a mechanism, there appears to be an excess of HCl and deficiency of chlorine in the products. This might result from reactions such as

$$Cl + CHCl_3 \rightarrow HCl + CCl_3; \quad \Delta H = -12 \text{ kcal}$$

followed by

$$CCl_3 + N \rightarrow CNCl + 2Cl; \quad \Delta H = -35 \text{ kcal.}$$

Other reactions that would lead to loss of chlorine at the expense of HCl production might be suggested, e.g.

$$N + N \cdot CHCl_3 \rightarrow N_2 + CHCl_3^*$$

and subsequent decomposition of the excited $CHCl_3$ to yield HCl and other products such as CCl_2, or free carbon, traces of which were observed.

The dichloromethane – active nitrogen reaction may be represented similarly to that of chloroform:

$$N + CH_2Cl_2 \rightarrow [N \cdot CH_2Cl_2] \rightarrow HCN + HCl + Cl; \quad \Delta H = -54 \text{ kcal}$$
$$\rightarrow CNCl + HCl + H; \quad \Delta H = -27 \text{ kcal}$$
$$\rightarrow CN + 2HCl; \quad \Delta H = -24 \text{ kcal.}$$

Since reaction of CN radicals with parent reactant appears not to have been appreciable (no optimum in $(CN)_2$ yield), and the amount of cyanogen formed was trivial, the third reaction must have been relatively unimportant. From the relative proportions of HCN and CNCl formed it may then be inferred that the first reaction was the predominant mode of attack.

Again, the rate of chlorine production was relatively low and HCl production relatively high. This suggests consumption of chlorine in reactions such as

$$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$$

and HCl production in reactions such as

$$H + CH_2Cl_2 \rightarrow HCl + CH_2Cl,$$

or

$$N + [N \cdot CH_2Cl_2] \rightarrow N_2 + CH_2Cl_2^*$$

followed by

$$CH_2Cl_2^* \rightarrow 2HCl + C.$$

As with chloroform, this last possibility is supported by the apparent formation of traces of free carbon.

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REACTIONS OF ALKOXY RADICALS

V. PHOTOLYSIS OF DI-*t*-BUTYL PEROXIDE[1]

GARNETT MCMILLAN AND M. H. J. WIJNEN[2]

ABSTRACT

The photolysis of di-*t*-butyl peroxide has been investigated over the temperature range 25° to 79° C. As reaction products were observed: acetone, *t*-butyl alcohol, methyl *t*-butyl ether, *i*-butylene oxide, ethane, methane, and carbon monoxide. The following reactions, involving the *t*-butoxy radical, have been studied:

$$(CH_3)_3CO \rightarrow CH_3COCH_3 + CH_3 \quad [2]$$

$$(CH_3)_3CO + CH_3 \rightarrow (CH_3)_3COCH_3 \quad [5]$$

$$(CH_3)_3CO + DtBP \rightarrow (CH_3)_3COH + R \quad [6]$$

An activation energy difference of $E_2 - E_6 = 3$ kcal has been obtained.

INTRODUCTION

Previous work (1, 2, 3) on the photolysis of di-*t*-butyl peroxide has established that the primary process consists of the breakage of the O—O bond, thus producing two *t*-butoxy radicals. It could also be shown that the *t*-butoxy radical is relatively unstable and decomposes according to reaction [2]:

$$(CH_3)_3CO \rightarrow CH_3COCH_3 + CH_3. \quad [2]$$

As most recent values for the activation energy of reaction [2] have been reported 11.2±2 (3) and 13.2±2.4 (4) kcal.

Such a value for E_2 would, however, indicate that especially at low temperatures the *t*-butoxy radical might survive long enough to take part in abstraction and recombination reactions. While the formation of *t*-butyl alcohol through hydrogen abstraction by *t*-butoxy radicals has been reported frequently (5, 6) no information was available regarding the activation energy for the abstraction of a hydrogen atom from di-*t*-butyl peroxide. In the photolysis of di-*t*-butyl peroxide a considerable amount of ethane is produced by recombination of methyl radicals, originating from reaction [2]. It seemed, therefore, likely that especially at low temperatures some methyl *t*-butyl ether might be produced via recombination reactions, although this compound had thus far not been reported among the reaction products.

In order to clear these questions the photolysis of di-*t*-butyl peroxide has been studied again.

EXPERIMENTAL

The apparatus is essentially the same as described previously (7). As a rule, a Hanovia S-500 medium pressure arc was employed as light source. The light intensity was varied by inserting wire-gauze screens between arc and cell. In some runs, marked as such in Table I under intensity, a BH-6 lamp, made by General Electric, was used. The effective light output of the BH-6 lamp is about three times that of the Hanovia S-500 arc.

After the photolysis, the reaction products and the excess di-*t*-butyl peroxide were cooled down to about −175° C. At this temperature CO, CH_4, and C_2H_6 were removed

[1]*Manuscript received May 8, 1958.*
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TABLE I

PHOTOLYSIS OF DI-*t*-BUTYL PEROXIDE[a]

Run No.	$[DtBP]_0$ Molecules/cc $\times 10^{-17}$	Time, sec	Intensity, relative %	R_x, in molecules/(sec cc) $\times 10^{-12}$						
				$R_{CH_3COCH_3}$	$R_{(CH_3)_3COH}$	$R_{(CH_3)_3COCH_3}$	$R_{(CH_3)_2CH_2CO}$	$R_{C_2H_6}$	R_{CH_4}	R_{CO}
				Temperature, 25° C						
12	5.14	720	BH-6	46.70	2.62	n.d.	2.00*	23.80	0.09	0.51
13	5.22	1800	100	25.40	1.08	n.d.	0.83*	13.21	0.70	0.83
14	5.43	1800	100	24.40	1.08	0.18	1.08	12.90	1.00	1.20
15	5.25	1800	100	24.85	1.06	n.d.	0.97*	12.75	0.75	0.69
16	5.25	1800	100	25.40	1.33	0.20	1.34	12.90	0.65	0.54
17	5.32	1800	100	25.10	1.08	0.17	1.10	12.90	0.64	0.68
18	5.41	16080	9	2.42	0.09		0.09	1.25	0.07	0.08
20	5.29	20100	9	2.18	0.07		0.10	1.12	0.06	0.06
21	2.74	2100	100	12.08	0.45	0.06	0.36	6.70	0.53	0.68
23	5.35	6480	30	5.97	0.26	0.02	0.26	3.06	0.19	0.16
				Temperature, 55° C						
33	4.80	10560	16	4.92	0.09		0.18	2.52	0.13	0.12
34	4.22	4620	30	7.92	0.16		0.28	4.09	0.24	0.22
35	4.07	1800	100	19.50	0.43		0.70	10.00	0.57	0.54
36	4.22	16320	9	2.06	0.04		0.10	1.05	0.06	0.05
37	4.41	360	BH-6	139.01	2.13	0.39	1.74	70.52	0.29	1.34
38	2.50	420	BH-6	65.20	2.80	0.24	2.27	33.50	0.62	1.26
40	3.21	600	BH-6	58.20	0.96	0.16	1.21	29.70	0.20	0.68
41	5.04	600	BH-6	88.80	1.41	0.26	1.86	45.20	0.20	0.88
42	2.96	720	BH-6	65.25	0.83	0.13	0.48	33.40	0.15	0.78
43	3.92	600	BH-6	44.70	1.41	0.14	1.10	22.91	0.15	0.63
44	3.92	600	BH-6	37.90	0.60	0.11	0.64	19.40	0.10	0.48
				Temperature, 79° C						
24	3.86	900	BH-6	63.00	1.93	0.10	2.20	33.71	0.56	2.51
25	3.86	1800	100	31.02	0.34		1.12	16.68	0.90	1.58
26	4.32	5400	30	10.86	0.12		0.35	5.79	0.34	0.53
27	4.54	17280	9	2.52	0.04		0.11	1.31	0.08	0.09
28	4.25	15700	9	2.04	0.03		0.13	1.07	0.08	0.09
29	4.05	1740	100	22.49	0.30		0.74	11.62	0.67	0.77
30	2.74	840	BH-6	43.60	0.59		0.08	22.84	0.08	1.07
31	4.32	9180	16	4.44	0.06		0.21	2.32	0.14	0.17
32	4.32	9240	16	4.44	0.07		0.21	2.32	0.15	0.18
39	2.35	420	BH-6	53.80	0.89		0.05	28.70	0.50	2.10

[a]Open spaces indicate that, under the given conditions, this compound was formed in amounts too small to allow its determination by mass-spectrometer analysis.

NOTE: Unless marked by *, data for *i*-butylene oxide are somewhat high owing to the presence of small amounts of methyl ethyl ketone.

by Toepler pump and sampled for mass-spectrometer analysis after their total volume had been measured. The liquid products were then separated from the excess undecomposed di-*t*-butyl peroxide by gas chromatography. A 6-ft-long general-purpose column C, obtained from Perkin–Elmer, was used. The column was operated at room temperature, using helium at a pressure of 10 lb as carrier gas. Under these conditions all reaction products come over within 25 minutes after introduction of the sample, while di-*t*-butyl peroxide is retained up to 67 minutes. The reaction products, thus separated from di-*t*-butyl peroxide, were trapped out and analyzed by mass spectrometer. In this way it was possible to determine the relative ratios in which the liquid products were formed although no absolute values are obtained.

It has been established previously (2, 5) that the ratio $(2R_{C_2H_6}+R_{CH_4})/R_{CH_3COCH_3}$ is equal to unity in the thermal and photolytic decomposition of di-*t*-butyl peroxide. This is easily understood if one realizes that one methyl radical is formed for every acetone

molecule produced by the thermal decomposition of the *t*-butoxy radical, according to reaction [2]. Taking into account that some methyl radicals are produced by secondary photolysis of acetone a more correct figure for the observed rate of acetone production is obtained by $R_{CH_3COCH_3} = 2(R_{C_2H_6}-R_{CO})+R_{CH_4}$. It is thus possible to calculate the rate of acetone production from the rates of methane, ethane, and carbon monoxide production. Since the relative ratio of acetone to other liquid products is determined by mass spectrometer, the rates of formation of all other products may be calculated.

In several runs a known amount of *i*-butane was added to the liquid products before mass-spectrometer analysis. Accurate data could thus be obtained for the production of acetone and other liquid products. In all instances data thus obtained for $R_{CH_3COCH_3}$ agreed with those calculated via the formula $R_{CH_3COCH_3} = 2(R_{C_2H_6}-R_{CO})+R_{CH_4}$.

It was not possible to discriminate by mass spectrometer between methyl ethyl ketone and *i*-butylene oxide, since the only available peak, yielding good resolution is *m/e* 72, common to both compounds. It was, however, possible to stop trapping of the reaction products, leaving the gas chromatography apparatus, before the appearance of methyl ethyl ketone. In this way, accurate data for the production of *i*-butylene oxide were obtained. These data indicated that peak *m/e* 72 was mainly due to the presence of *i*-butylene oxide. Since neither of these two compounds are of extreme interest in the present discussion, data reported in Table I for *i*-butylene oxide have been calculated on the assumption that no methyl ethyl ketone was formed.

The conversion has been kept below 5% of the starting material. The di-*t*-butyl peroxide used in this investigation was obtained from Shell Chemical Corporation and was distilled under reduced pressure, a small middle fraction being retained. Gas chromatographic analysis indicated it to be more than 99% pure.

RESULTS AND DISCUSSION

Data, obtained by photolyzing di-*t*-butyl peroxide at different temperatures and light intensities are reported in Table I. The following reactions have been considered to explain the formation of acetone, *t*-butyl alcohol, methyl-*t*-butyl ether, *i*-butylene oxide, ethane, and methane:

$$(CH_3)_3COOC(CH_3)_3 + h\nu \rightarrow 2(CH_3)_3CO \quad [1]$$

$$(CH_3)_3CO \rightarrow CH_3COCH_3 + CH_3 \quad [2]$$

$$2(CH_3)_3CO \rightarrow (CH_3)_3COH + (CH_3)_2CH_2CO \quad [3]$$

$$CH_3 + (CH_3)_3CO \rightarrow CH_4 + (CH_3)_2CH_2CO \quad [4]$$

$$CH_3 + (CH_3)_3CO \rightarrow (CH_3)_3COCH_3 \quad [5]$$

$$(CH_3)_3CO + DtBP \rightarrow (CH_3)_3COH + (CH_3)_3COOC(CH_3)_2CH_2 \quad [6]$$

$$(CH_3)_3COOC(CH_3)_2CH_2 \rightarrow (CH_3)_3CO + (CH_3)_2CH_2CO \quad [7]$$

$$2CH_3 \rightarrow C_2H_6 \quad [8]$$

$$CH_3 + DtBP \rightarrow CH_4 + (CH_3)_3COOC(CH_3)_2CH_2 \quad [9]$$

However, in addition to the reaction products mentioned above, also carbon monoxide and traces of methyl ethyl ketone were observed. Table I clearly shows that acetone is the most abundant reaction product and it seems logical to accept, as other authors (3) did, that CO and $C_2H_5COCH_3$ are formed by secondary photolysis of acetone. The following reactions are therefore added:

$$CH_3COCH_3 + h\nu \rightarrow CH_3 + CH_3CO \quad [10]$$

$$CH_3 + CH_3CO \rightarrow CH_3COCH_3 \quad [11]$$

$$CH_3 + CH_3CO \rightarrow CH_4 + CH_2CO \quad [12]$$

$$CH_3CO \rightarrow CH_3 + CO \quad [13]$$

$$R + CH_3COCH_3 \rightarrow CH_2COCH_3 + RH \quad [14]$$

$$CH_3 + CH_2COCH_3 \rightarrow C_2H_5COCH_3 \quad [15]$$

The following equations may be derived from this mechanism:

$$R_{CH_3COCH_3} \times R^{\frac{1}{2}}_{C_2H_6}/R_{CH_3OC(CH_3)_3} = k_2k_8^{\frac{1}{2}}/k_5 \quad [I]$$

and

$$R_{(CH_3)_3COH}/R^2_{CH_3COCH_3} = k_3/k_2^2 + k_6/k_2[DtBP]/R_{CH_3COCH_3}, \quad [II]$$

where R_x is the rate of production of the compound x.

Owing to secondary reactions involving acetone, $R_{CH_3COCH_3}$ is not correctly given by measuring the observed rate of acetone production. Some of the originally formed acetone decomposed to give CO and methyl radicals, some reacted to form methyl ethyl ketone. The amount of methyl ethyl ketone is, however, smaller than 1% of the originally formed acetone and may therefore be neglected. The amount of acetone decomposed to CO and methyl radicals is given by the rate of CO production. In calculating equations [I] and [II] the rate of acetone production by reaction [2] is therefore given by the sum of the *observed* rate of acetone production and the rate of production of carbon monoxide. At room temperature a constant value was obtained for equation [I], indicating $k_2k_8^{\frac{1}{2}}/k_5 = 5.1 \pm 0.5 \times 10^3$ in molecules$^{\frac{1}{2}}$/(sec$^{\frac{1}{2}}$ cc$^{\frac{1}{2}}$). Equation [I] involves the reaction products: acetone, ethane, and methyl *t*-butyl ether. Acetone and ethane are the major reaction products in the photolysis of di-*t*-butyl peroxide. Methyl *t*-butyl ether is, however, formed in trace amounts only. As a matter of fact, the largest amount of ether observed did not exceed 3×10^{-3} ml of gas at n.t.p. This undoubtedly explains why this product was not observed by previous investigators. With increasing temperature, the production of ether decreases, mainly owing to an increased decomposition of the *t*-butoxy radical into acetone and methyl radicals via reaction [2]. The results obtained for $k_2k_8^{\frac{1}{2}}/k_5$ show, therefore, considerable scatter at 55° C, as indicated in Table II. At 79° C the amount of ether produced was too small to allow its determination by mass-spectrometer analysis.

TABLE II

RATIOS OF RATE CONSTANTS

Temperature, °C	$10^{19}k_6/k_2$	$10^{-8}k_2k_8^{\frac{1}{2}}/k_5$, molecules$^{\frac{1}{2}}$/(cc$^{\frac{1}{2}}$ sec$^{\frac{1}{2}}$)
25	0.72	5.1
55	0.45	21±6
79	0.32	—

It is obvious that an activation energy, determined from data at two temperatures only, should be taken with the utmost reservation. It is nevertheless interesting to point out that our data indicate a value of 9±2 kcal for the activation energy of reaction [2]. This value agrees within experimental error with data obtained by Volman and Graven (3), who reported $E_2 = 11.2 \pm 2$ kcal.

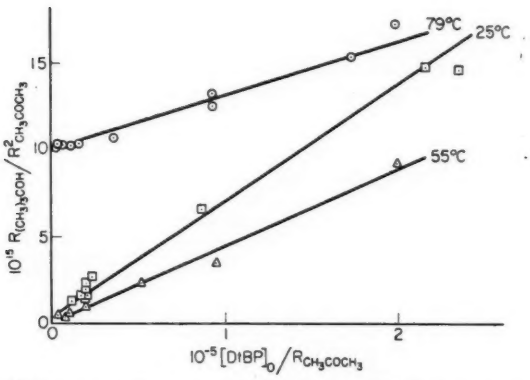

FIG. 1. Plot of $10^{15}R_{(CH_3)_3COH}/R^2_{CH_3COCH_3}$ versus $10^{-5}[DtBP]_0/R_{CH_3COCH_3}$ at various temperatures.

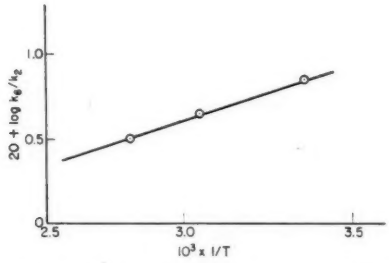

FIG. 2. Plot of $20+\log k_6/k_2$ versus $10^3 \times 1/T$.

Equation [II] is plotted in Fig. 1 for the temperatures 25, 55, and 79° C. The origin on the ordinate has been displaced by 10 units for the data at 79° C. Values obtained for k_6/k_2 from Fig. 1 are given in Table II. A plot of log k_6/k_2 in Fig. 2 gives an activation energy difference of $E_2 - E_6 = 3$ kcal.

No intercepts are observed when plotting equation [II] (Fig. 1) for the temperatures 55° and 79° C. It is difficult to decide whether the intercept observed at 25° C is real. The absence of an intercept would prove that reaction [3], the disproportionation of two *t*-butoxy radicals, would not occur. It may, however, be concluded that $k_3/k_2^2 \leqslant 0.5 \times 10^{-15}$ in molecules^{-1}/(sec^{-1} cc^{-1}). From this conclusion it is possible to calculate the maximum amounts of *t*-butyl alcohol and *t*-butylene oxide formed by reaction [3]. Such calculations indicate that *t*-butyl alcohol is mainly, if not only, formed by abstraction reaction [6] rather than by disproportionation of *t*-butoxy radicals. These calculations also indicate that, even at 25° C, *i*-butylene oxide is mainly, if not only, formed by decomposition of the $(CH_3)_3COO(CH_3)_2CH_2$ radical as suggested by reaction [7].

A value of 11.3 kcal has been reported (8) for the activation energy of reaction [9], the abstraction of a hydrogen atom from di-*t*-butyl peroxide by methyl radicals. Accepting our value of $E_2 - E_6 = 3$ kcal and $E_2 = 11.2\pm$ kcal, as reported by Volman and Graven, the data indicate that less energy is required for the abstraction of a hydrogen atom from di-*t*-butyl peroxide by *t*-butoxy radicals than for the similar reaction by methyl radicals. A similar observation has been made regarding the case of abstraction reactions by methoxy and methyl radicals (9).

ACKNOWLEDGMENTS

The authors wish to express their sincere thanks to Dr. H. D. Medley for his constant interest in the fundamental research program of this laboratory. They also thank Mr. R. W. Jarret and Mr. R. M. Guedin for calculation and interpretation of the mass-spectrometer data.

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THE EXTRACTION OF PLUTONIUM FROM NEUTRON-IRRADIATED URANIUM BY URANIUM TRICHLORIDE AND BY MAGNESIUM CHLORIDE[1]

D. E. McKenzie,[2] W. L. Elsdon, and J. W. Fletcher

ABSTRACT

The extraction of plutonium from neutron-irradiated uranium by uranium trichloride and by magnesium chloride has been examined in the temperature range 1150° to 1250° C. The results of the uranium trichloride experiments have been used to evaluate the standard free-energy change of the equilibrium reaction $UCl_3 + Pu \leftrightharpoons PuCl_3 + U$. These free-energy values have been used to predict the plutonium extraction in the magnesium chloride experiments on the assumption that the uranium trichloride, continuously formed from the non-equilibrium reaction $3/2MgCl_2 + U \rightarrow UCl_3 + 3/2Mg$, rapidly established the above equilibrium with the plutonium in the uranium. Agreement between predicted and experimental results supports this assumption.

A preliminary study of the kinetics of the $MgCl_2$–U reaction showed that the initial rate of reaction is controlled by the distillation of magnesium metal from the reaction zone.

INTRODUCTION

In previous papers, the separation of plutonium from neutron-irradiated uranium by volatilization (1) and by liquid silver extraction (2) was described. Another possible technique for achieving this important separation is by reaction of plutonium with molten inorganic salts, as represented in the following equilibrium expression,

$$MX + Pu \leftrightharpoons PuX + M.$$

The plutonium salt formed by the reaction enters the salt phase and is thus separated from the uranium metal. This method has been examined by a number of investigators (3, 4) using uranium fluorides. The present paper describes an investigation of the extraction of plutonium by uranium trichloride and by magnesium chloride.

High-temperature thermodynamic data may be used to predict the distribution of plutonium between the salt and metal phases. From the data on the free energy of formation, the standard free-energy change accompanying the reactions may be calculated for a given temperature. These values may be used to obtain the equilibrium constant for that temperature. Using the mass-action expression for the equilibrium constant, the distribution of plutonium between the two phases may be calculated.

Since only estimated values for the free energies of formation of liquid uranium and plutonium chlorides are available (5, 6), the distribution equilibria are a useful check on the reliability of the available data for these compounds. Besides testing the available thermodynamic data, the above calculations have been reversed to give, from the experimental data, new equilibrium constants, and hence, standard free-energy changes accompanying the reactions. A similar procedure has been used by Buyers to determine the free energy of formation of plutonium trifluoride (7). These new values have been used to predict the distribution of plutonium in the experiments with magnesium chloride.

EXPERIMENTAL

Materials and Apparatus

The neutron-irradiated uranium was cut from natural uranium fuel rods which had been irradiated in the NRX reactor and allowed to decay for 3 years. The concentration

[1]*Manuscript received May 8, 1958.*
Contribution from Chemistry and Metallurgy Division, Research Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada.
Issued as A.E.C.L. No. 656.
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of plutonium in this material was 0.025%. Uranium trichloride was prepared from uranium metal by passing hydrogen chloride over the hydride (8). Considerable care to exclude moisture and air was required to obtain a pure product. Anhydrous magnesium chloride was obtained by carefully heating C.P. grade ammonium magnesium chloride hexahydrate in a current of dry hydrogen chloride to remove water, followed by further heating in vacuum to remove ammonium chloride. Magnesium analyses of the product gave 25.67 and 25.35% Mg, calculated 25.54%. The chlorides were stored and handled in a dry nitrogen atmosphere.

The uranium and salt, contained in an alumina crucible ("Triangle" recrystallized alumina, Morganite Carbon Products Canada Limited, 195 Eastern Ave., Toronto 2, Ontario), were heated by a tungsten wire coil surrounded by thermal and radiation shields. The assembly was mounted in a glass bulb which could be evacuated by diffusion and mechanical pumps (1). Temperatures were measured with a platinum, platinum – 10% rhodium thermocouple which was coiled in the heating zone as a seat for the crucible containing the charge. The thermocouple was calibrated to give the temperature of the charge by melting various pure metals in the apparatus. The temperature measurements were accurate to ±5° C.

Procedure and Analyses

For an experiment, the uranium was etched in acid to remove approximately 25% of its weight for a reference solution, then washed in water and acetone. Weighed amounts of the chloride and of neutron-irradiated uranium, in an alumina crucible, were placed in the apparatus. The glass bulb was pumped down to a pressure of 10^{-5} mm Hg or less and then the crucible was heated to 300° C for further degassing. After admitting welding grade argon to a pressure of 1 atmosphere, the charge was heated to temperature. The salt and uranium were contacted for 30 minutes in all runs except those where time was the variable to be studied.

After contacting, the charge was cooled in an argon atmosphere, separated from the crucible, and the salt phase dissolved or washed away from the metal billet. In each experiment the complete phase was dissolved for analysis. The solutions were analyzed for uranium (9) and magnesium (10) spectrophotometrically; plutonium was determined using standard radiochemical procedures. Plutonium recoveries of 95% or better were obtained in all runs.

RESULTS AND DISCUSSION

The Extraction of Plutonium with Uranium Trichloride

On contacting the liquid phases of uranium trichloride and neutron-irradiated uranium the following equilibrium is established:

$$UCl_3 + Pu \rightleftharpoons PuCl_3 + U.$$

The literature values of thermodynamic data listed in Table I were used to calculate the equilibrium constants for the above equilibrium. The distribution of plutonium between salt and metal was then predicted on the assumptions that plutonium behaves ideally in molten neutron-irradiated uranium and that the product plutonium trichloride dissolves to form an ideal solution in uranium trichloride. Evidence at higher temperatures for the former assumption has been obtained in previous work (1, 3), while the isomorphism of the trichlorides and the proximity of plutonium and uranium in the actinide series are supporting evidence for the validity of the latter.

The extraction of plutonium was examined for various U/UCl_3 mole ratios (Table II)

and also at various temperatures (Table III). The proportions of the original plutonium remaining in the salt and in the metal phase are listed in the tables. The calculations using the thermodynamic data give directly the proportion of the original plutonium remaining in the uranium phase and these are listed in the last column of each table.

TABLE I

THERMODYNAMIC DATA FOR UCl_3 AND $PuCl_3$

Compound	Reference No.	$(\Delta F - \Delta H_{298})/T$(calories/degree) 500° K	1000° K	1500° K	ΔH_{298} (kcal)	Melting point (° K)
UCl_3	5	53.51 (s)	51.65 (s)	49 (l)	−213.5	1108
$PuCl_3$	6	54 (s)	53 (s)	50 (l)	−229.3	1033

Although the calculated values (Table II) for plutonium remaining in the uranium phase are close enough to the experimental values to be useful in making predictions, the experimental results at 1200° C are consistently lower (i.e. less plutonium in the uranium phase) than the predictions. Also, in Table III, there is excellent agreement for experiments at 1160° C but the data show a trend of increasing extraction with temperature, which is the reverse of that predicted by the thermodynamic data. In view of these discrepancies and the fact that the thermodynamic data were estimated, it seemed worth while to use the experimental data and the assumptions of ideality to calculate equilibrium constants and standard free-energy changes accompanying this reaction. The results of these calculations are shown in Table IV. The table shows for each temperature the "average" value for the equilibrium constant from which the standard free-energy

TABLE II

EFFECT OF MOLE RATIO U/UCl_3 ON EXTRACTION OF PLUTONIUM AT 1200° C

Wt U (g)	Wt UCl_3 (g)	Mole ratio U/UCl_3	Pu distribution (% original) Exptl. Salt	Exptl. U	Calc. U
19.100	1.000	27.63	84.8	12.7	18.3
15.928	0.883	26.10	89.2	11.5	17.4
15.057	1.000	21.78	88.2	10.6	15.0
9.289	1.002	13.41	91.1	6.9	9.8
5.909	1.186	7.20	95.0	5.6	5.5

TABLE III

EFFECT OF TEMPERATURE ON EXTRACTION OF PLUTONIUM BY URANIUM TRICHLORIDE

Mole ratio $U/UCl_3 \approx 14$

Temperature (° C)	Mole ratio U/UCl_3	Pu distribution (% original) Exptl. Salt	Exptl. U	Calc. U
1160	15.14	90.6	9.4	9.5
1160	15.00	90.5	8.9	9.4
1200	13.41	91.1	6.9	9.8
1250	14.21	93.0	7.7	12.0
1280	13.96	94.2	4.5	13.0

TABLE IV

EXPERIMENTAL VALUES FOR THE EQUILIBRIUM CONSTANTS AND ΔF°'S FOR THE REACTION $UCl_3 + Pu \leftrightharpoons PuCl_3 + U$

Temperature (° C)	Equilibrium constant (K)	K_{av}	ΔF° (kcal) (Experimental)	ΔF° (kcal) (Brewer *et al.*)
1160	154	150	−14.3	−14.4
	146			
1200	191	189	−15.3	−14.1
	184			
	181			
	200			
1250	170	170	−15.5	−14.1
1280	294	294	−17.5	−14.0

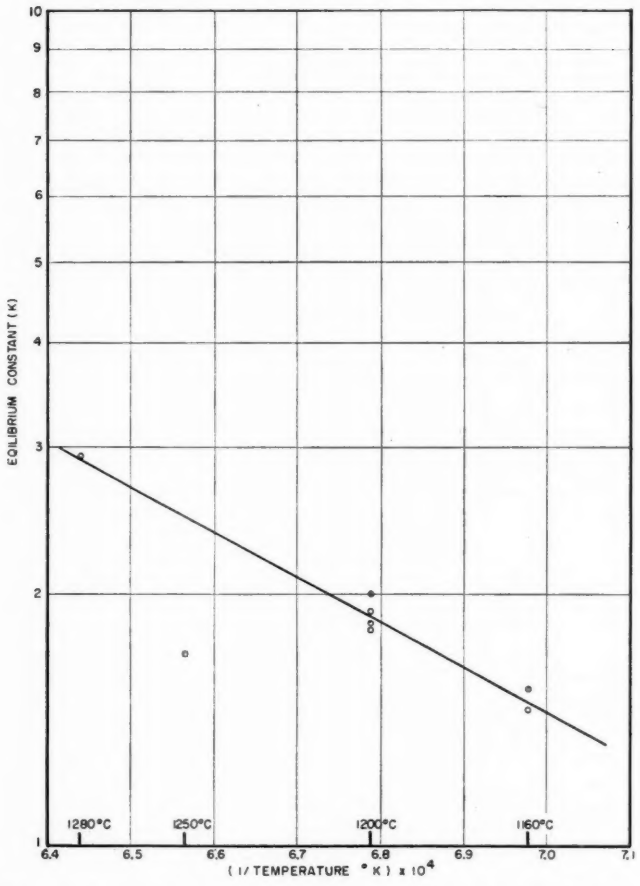

FIG. 1. The effect of temperature on the experimentally determined equilibrium constants for the reaction $UCl_3 + Pu \leftrightharpoons PuCl_3 + U$.

change for that temperature has been evaluated. This ΔF° is then compared with the previous estimate of Brewer *et al.* (5, 6). (For this comparison the estimates are listed to three significant figures although Brewer *et al.* give only two.)

As a test of the internal consistency of the data, a plot of log K vs. $1/T$ should yield a straight line. This plot is shown in Fig. 1. Although the result at 1250° C is low, the other data are reasonably consistent and may be represented, approximately, by the equation $\log K = 5.96-(5.42\times10^3/T)$. From the slope of this line the enthalpy change accompanying the reaction $UCl_3 + Pu \leftrightharpoons PuCl_3 + U$ at about 1220° C is calculated to be 24.8 kcal.

The Reaction of Uranium Metal and Magnesium Chloride

Molten magnesium chloride in contact with molten uranium reacts according to the following equation:

$$3/2MgCl_2 + U \rightarrow UCl_3 + 3/2Mg.$$

Since magnesium chloride has a higher free energy of formation (i.e. more negative) than uranium trichloride, it would be expected that the reaction proceeds because the experiments were performed under conditions which permitted continuous distillation of magnesium from the reaction zone. It might be anticipated, further, that the initial rate of reaction will depend upon the surface area of uranium exposed to the salt. As the reaction proceeds, however, the rate will decrease owing to the accumulation of the reaction product, uranium trichloride, in the salt phase. These general expectations have been found to be correct.

The initial reaction rates have been measured using both neutron-irradiated uranium and natural uranium at a number of temperatures; the data are summarized in Table V and plotted as log rate (grams of U reacted/hr cm² U surface) vs. $1/T$ in Fig. 2. The results have been treated by the least squares method to give the equation: log rate (grams of U reacted/hr cm² U surface) $= 4.76-(7.16\times10^3/T)$. From the slope of this line an activation energy of 32.8 kcal has been calculated for the rate-controlling step of the initial process. This activation energy may be compared with the value of 32.3 kcal per mole, the heat of vaporization of magnesium metal at 1200° C (11). This agreement is good evidence that the initial rate of the reaction of uranium metal and magnesium chloride is controlled by the distillation of magnesium metal from the reaction zone.

TABLE V

THE EFFECT OF TEMPERATURE ON THE INITIAL REACTION RATE OF $MgCl_2$ AND URANIUM METAL

Temperature (° C)	Wt U (g)	Wt $MgCl_2$ (g)	U surface area (cm²)	Time (min)	U reacted (g)	U reacted (g/hr)
Neutron-irradiated uranium						
1150	7.825	1.561	1.2	40	0.409	0.613
1200	7.302	1.517		30	0.469	0.939
1245	9.268	1.788		30	0.667	1.335
Natural uranium						
1150	12.826	2.565	1.9	30	0.495	0.991
1180	13.649	3.631		30	0.700	1.400
1200	13.391	3.754		33	0.808	1.470
1260	13.701	3.917		30	1.124	2.248
1285	12.807	3.659		30	1.362	2.725

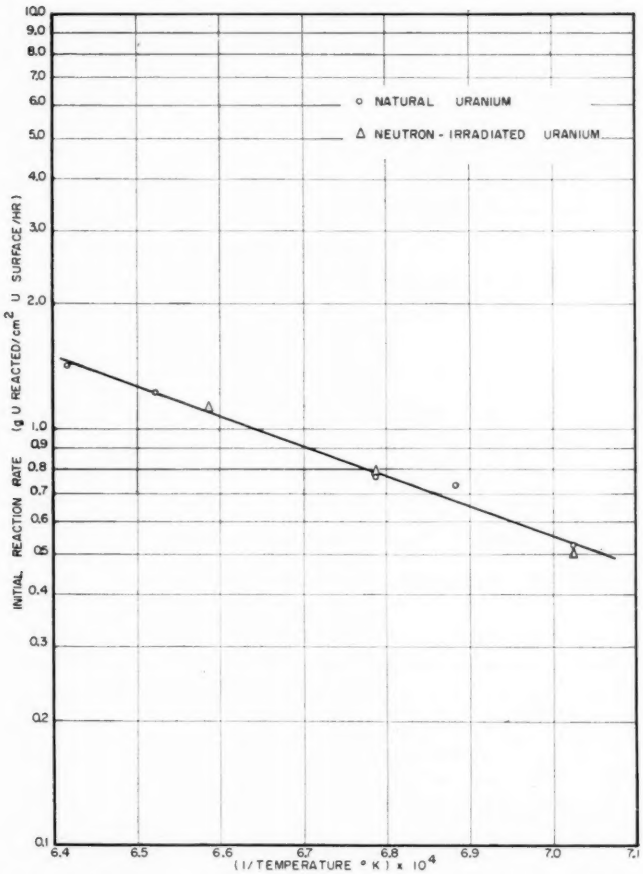

FIG. 2. The effect of temperature on the initial rate of reaction between magnesium chloride and uranium metal.

The Extraction of Plutonium in the Magnesium Chloride Experiments

For these experiments, the following reactions occur on contacting magnesium chloride with molten neutron-irradiated uranium:

$$3/2MgCl_2 + U \rightarrow UCl_3 + 3/2Mg \quad [1]$$

$$3/2MgCl_2 + Pu \rightarrow PuCl_3 + 3/2Mg \quad [2]$$

$$UCl_3 + Pu \leftrightharpoons PuCl_3 + U. \quad [3]$$

The experiments were performed under a pressure of one atmosphere of argon and at a temperature above the boiling point of magnesium metal. Thus, since the temperature of the glass bulb surrounding the reaction crucible was considerably below the melting point of magnesium, the magnesium continuously distilled from the reaction zone and equilibrium with respect to reactions [1] and [2] was not reached. To calculate the extraction of plutonium using thermodynamic data, it was assumed that reaction [3], which does no involve tvolatile components, was in equilibrium at all times, and that uranium trichloride was dissolved in an inert diluent, magnesium chloride.

On this basis, the equilibrium constants, calculated from the expression derived for the uranium trichloride experiments, were used to predict the extraction of plutonium in the magnesium chloride experiments. At the conclusion of an experiment the concentration of uranium trichloride in the salt phase was determined (by chemical analysis) and substituted into the mass-action expression to calculate the plutonium distribution, again, assuming ideal solution behavior in the salt and metal phases.

The extraction of plutonium has been examined at three temperatures (Table VI) and for various times (Table VII). The tables show the mole fraction of uranium trichloride in the salt and the proportions of original plutonium in the salt and in the metal at the end of each experiment. The latter is compared with the calculated value for plutonium remaining in the uranium.

TABLE VI

EFFECT OF TEMPERATURE ON EXTRACTION OF PLUTONIUM BY MAGNESIUM CHLORIDE

Contacting time = 30 minutes

Temperature (° C)	Wt U (g)	Wt $MgCl_2$ (g)	Final UCl_3 in salt		Pu distribution (% original)		
					Exptl.		Calc.
			% Original U	Mole fraction	Salt	U	U
1150	7.825	1.561	5.2	0.11	87.3	10.0	11.3
1200	7.302	1.517	6.4	0.13	91.4	9.0	7.0
1245	9.268	1.788	7.2	0.15	91.8	8.0	5.3

TABLE VII

EFFECT OF CONTACTING TIME ON EXTRACTION OF PLUTONIUM BY MAGNESIUM CHLORIDE AT 1200° C

Time (min)	Wt U (g)	Wt $MgCl_2$ (g)	Final UCl_3 in salt		Pu distribution (% original)		
					Exptl.		Calc.
			% Original U	Mole fraction	Salt	U	U
10	9.941	1.028	1.7	0.06	56.2	40.3	22.8
30	9.315	1.045	2.5	0.10	84.3	18.0	16.7
60	10.174	1.126	3.4	0.12	90.0	10.9	12.5
120	9.170	1.026	6.5	0.21	92.9	6.1	6.6

The reasonable agreement of the calculated and experimental results for contacting times of thirty minutes or longer provides some support for the assumptions used in making the calculations. Thus, the distribution of plutonium can be predicted from the concentration of uranium trichloride in the salt phase by assuming that the reaction between plutonium and uranium trichloride is at equilibrium even though magnesium chloride and uranium are still reacting. The results for the first experiment listed in Table VII indicate that this assumption does not hold for contacting times of less than thirty minutes.

Two additional experiments were performed at 1140° C and an argon pressure of 100 p.s.i.g. The objective in these experiments was to prevent the formation of uranium trichloride by preventing the distillation of magnesium metal. The data are summarized in Table VIII. While the application of pressure to this system did not completely prevent distillation, the results show that the rate of distillation was reduced, since there was considerably less uranium trichloride formed than in other 30-minute experiments

(e.g. Table VI). Similarly, it would be expected that the rate of reaction between magnesium chloride and plutonium would be reduced below that for experiments at one atmosphere pressure. However, the reduction in the rate of this reaction would not be expected to influence the extraction equilibrium, since it is assumed that this equilibrium is controlled by the uranium trichloride concentration. The reasonable agreement between calculated and experimental results in these experiments provides additional support for this assumption.

TABLE VIII

EXTRACTION OF PLUTONIUM BY MAGNESIUM CHLORIDE AT 1140° C AND 100 P.S.I.G. ARGON

Contacting time = 30 minutes

Wt U (g)	Wt $MgCl_2$ (g)	Final UCl_3 in salt		Pu distribution (% original)		
				Exptl.		Calc.
		% Original U	Mole fraction	Salt	U	U
9.753	2.029	1.74	0.034	65.1	33.3	30.0
13.370	2.400	1.49	0.035	60.0	39.3	33.4

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of Mr. A. S. Denovan, who performed most of the analyses required in this study.

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CYCLOHEXANE COMPOUNDS

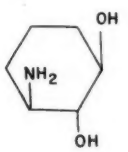
II. SYNTHESIS AND STRUCTURE OF TWO STEREOISOMERIC 3-AMINO-1,2-CYCLOHEXANEDIOLS[1,2]

R. A. B. Bannard and L. R. Hawkins

ABSTRACT

The stereoisomeric 1-ethoxy-2,3-epoxycyclohexanes were prepared from 1-ethoxycyclohexene-2 via 1-ethoxycyclohexene-2 bromohydrin. Ammonolysis of the lower- and higher-boiling oxides furnished 1α-ethoxy-2β-hydroxy-3α-aminocyclohexane and 1α-ethoxy-2α-hydroxy-3β-aminocyclohexane respectively. In a similar manner, 1α-methoxy-2β-hydroxy-3α-aminocyclohexane and 1α-methoxy-2α-hydroxy-3β-aminocyclohexane were obtained from 1-methoxycyclohexene-2 via 1-methoxycyclohexene-2 bromohydrin and the stereoisomeric 1-methoxy-2,3-epoxycyclohexanes. Ether cleavage of 1α-ethoxy- and 1α-methoxy-2β-hydroxy-3α-aminocyclohexane gave 3α-amino-1α,2β-cyclohexanediol hydrobromide, from which the free base was obtained. 3β-Amino-1α,2α-cyclohexanediol was prepared similarly from 1α-ethoxy- and 1α-methoxy-2α-hydroxy-3β-aminocyclohexane. The stereochemistry of the 3-amino-1,2-cyclohexanediols, 1-alkoxy-2-hydroxy-3-aminocyclohexanes, and 1-alkoxy-2,3-epoxycyclohexanes has been elaborated.

In 1947 Mousseron and co-workers (1, 2, 3) prepared an ethoxyaminocyclohexanol of unknown structure by ammonolysis of 1-ethoxy-2,3-epoxycyclohexane, and in 1952, McCasland *et al.* (4) obtained a similar substance, m.p. 132–134°, in the same manner as Mousseron *et al.* (1, 2, 3). The compound was characterized as the N-*p*-nitrobenzoyl derivative, m.p. 201–203°, and was converted on ether cleavage with hydrobromic acid



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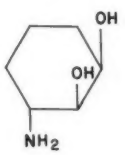

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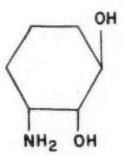

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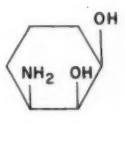

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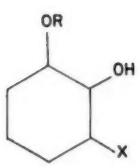

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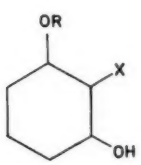

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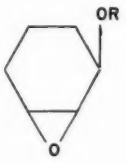
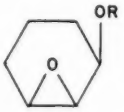
[1]*Manuscript received April 15, 1958.*
Contribution from Defence Research Chemical Laboratories, Ottawa, Canada. Issued as D.R.C.L. Report No. 273. Presented in part at the 41st Annual Conference of the Chemical Institute of Canada, Toronto, May 26–28, 1958.
[2]*For Part I of this series see reference 12.*

to an aminocyclohexanediol hydrobromide, m.p. 167–168°. The N-*p*-nitrobenzoyl derivative of the latter compound (m.p. 182–183°) rapidly consumed 1 mole of periodate, thus showing the aminediol to be a 3-amino-1,2-cyclohexanediol. McCasland *et al.* (4) did not assign a stereochemical structure to the substance but pointed out that of the four possible structures (I to IV) only I and II are probable, since oxide ring opening usually yields *trans*-oriented products (5, 6). The present communication describes the synthesis and assignment of structure to two isomeric 3-amino-1,2-cyclohexanediols and to the 1-alkoxy-2,3-epoxycyclohexanes and 1-alkoxy-2-hydroxy-3-aminocyclohexanes used as intermediates in their preparation.

Mousseron *et al.* (1, 2, 3) and McCasland *et al.* (4) had prepared 1-ethoxy-2,3-epoxycyclohexane, either by peracid oxidation of 1-ethoxycyclohexene-2, or by the action of aqueous alkali on 1-ethoxycyclohexene-2 chlorohydrin (V or VI; R = C_2H_5, X = Cl). The chlorohydrin, which was obtained (1, 3, 4) by interaction of monochlorourea (7, 8) and 1-ethoxycyclohexene-2, was considered by McCasland *et al.* (4) to possess structure VI (R = C_2H_5, X = Cl). No proof was submitted in support of this structure nor was it demonstrated that the chlorohydrin thus obtained consists of a mixture of isomers. In 1942 Moir (9), McRae (10), and co-workers studied the reaction between 1-methoxycyclohexene-2 and monochlorourea, and found that a mixture of isomeric chlorohydrins (V or VI; R = CH_3, X = Cl) was formed together with 1-methoxycyclohexene dichloride. It did not prove possible to separate the isomeric chlorohydrins from each other or completely from the dichloride by fractional distillation. The chlorohydrin mixture on treatment with aqueous alkali yielded a mixture of stereoisomeric 1-methoxy-2,3-epoxycyclohexanes (VII and VIII; R = CH_3), demonstrating the presence of at least two isomeric chlorohydrins in the mixture. Somewhat later, but prior to the work of Mousseron *et al.* (1, 3) and McCasland *et al.* (4), Fenton (11) showed that 1-ethoxycyclohexene-2 on treatment with monochlorourea led to a mixture of isomeric chlorohydrins (V or VI; R = C_2H_5, X = Cl) which in turn gave two stereoisomeric 1-ethoxy-2,3-epoxycyclohexanes (VII and VIII; R = C_2H_5). Fenton (11) did not make it clear whether or not 1-ethoxycyclohexene dichloride was present in the chlorohydrin mixture. Repetition of Fenton's work revealed that 1-ethoxycyclohexene dichloride is indeed present. Numerous attempts to separate the chlorohydrin–dichloride mixture by fractional distillation proved fruitless (see Table III).



(VII)



(VIII)

The presence of dichlorides in the 1-alkoxycyclohexene-2 chlorohydrins detracts from their usefulness for preparation of the corresponding oxides, since both the *trans*-, or lower-boiling, oxide (VII) and the *cis*-, or higher-boiling, oxide (VIII) were contaminated with chlorinated substances (10). Furthermore, the fact that the isomeric chlorohydrins are not readily separable makes them impractical as intermediates for preparation of

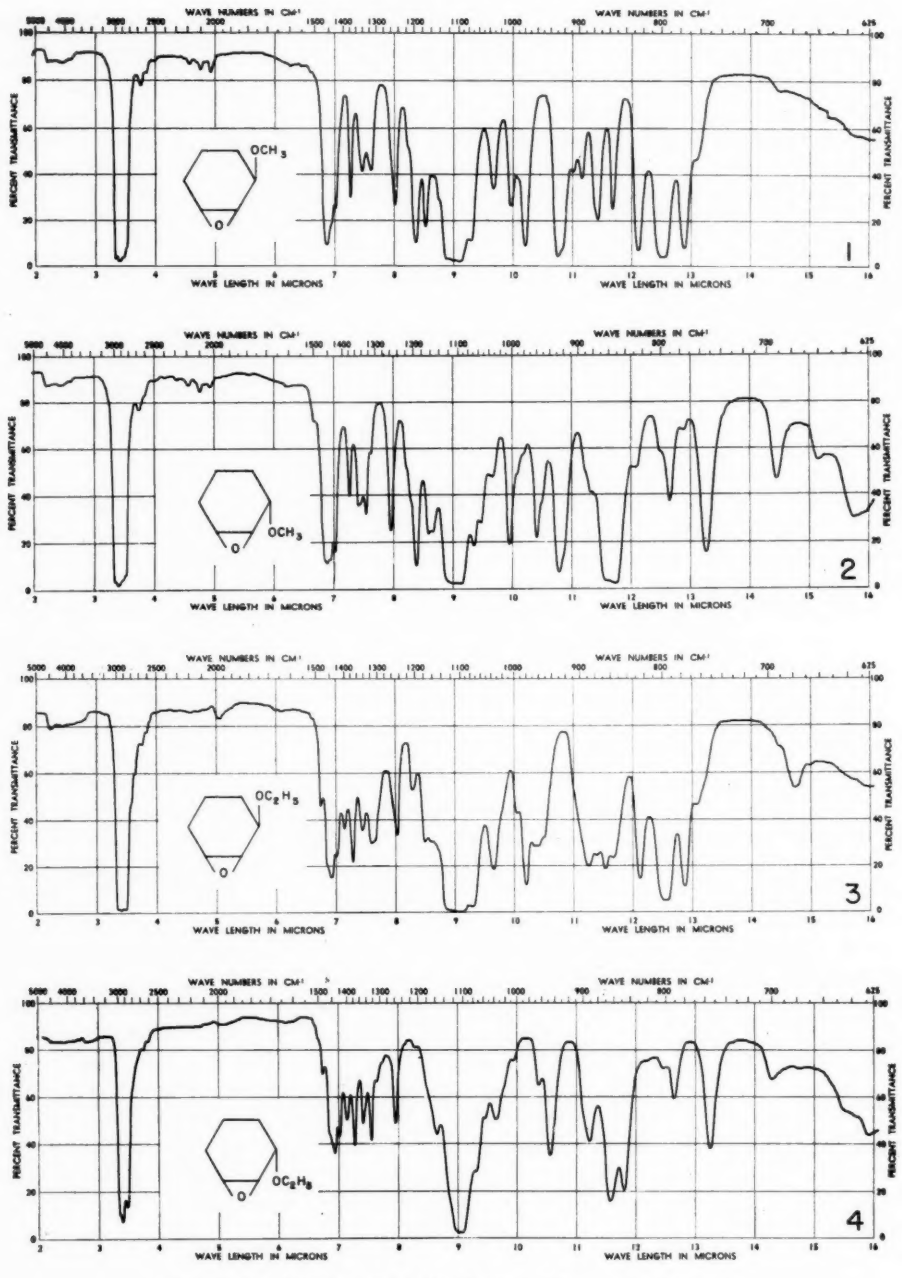
the 1-ethoxy-2-hydroxy-3-aminocyclohexanes by direct ammonolysis (12) because it has been found in the present investigation that separation of the resultant stereoisomeric amines is too laborious. Attention was therefore turned to preparation of the corresponding bromohydrins in the hope that either or both disadvantages characteristic of the chlorohydrins would be eliminated.

For many years the structures of the 1-methoxy-2,3-epoxycyclohexanes remained unassigned. Recently, however, it has been shown by Lemieux, Kullnig, and Moir (13) via proton magnetic resonance spectroscopy on the 1,3-dimethoxy-2-acetoxycyclohexanes resulting from acetylation of the products of methanolysis of the 1-methoxy-2,3-epoxycyclohexanes, that the lower-boiling isomer (the so-called α-isomer (10)) has the *trans*-configuration and the higher-boiling isomer (the so-called β-isomer (10)) the *cis*-configuration. This work, however, still left unsettled the configurations of Fenton's 1-ethoxy-2,3-epoxycyclohexanes. It will be demonstrated in the sequel that in this case also, the lower-boiling oxide is the *trans*-isomer and the higher-boiling oxide the *cis*-isomer.

1-Methoxy- and 1-ethoxycyclohexene-2 were prepared by modification of the method of Gogek *et al.* (14). 1-Methoxycyclohexene-2 on treatment with N-bromosuccinimide in aqueous suspension (cf. Guss and Rosenthal (15)) gave a mixture of isomeric 1-methoxycyclohexene-2 bromohydrins (V or VI; R = CH_3, X = Br) in 77% yield, uncontaminated with the corresponding dibromide. In a similar manner the mixed 1-ethoxycyclohexene-2 bromohydrins (V or VI; R = C_2H_5, X = Br) were obtained in 85% yield also free of dibromide. It did not prove possible to separate the isomeric bromohydrins by fractional distillation. However, the bromohydrin mixtures proved much superior to the chlorohydrin–dichloride mixtures as intermediates for preparation of the stereoisomeric 1-alkoxy-2,3-epoxycyclohexanes (VII and VIII).

1-Methoxycyclohexene-2 bromohydrin (V or VI; R = CH_3, X = Br) on treatment with aqueous sodium hydroxide gave an 84% yield of the stereoisomeric *dl*-1-methoxy-2,3-epoxycyclohexanes (VII and VIII; R = CH_3), which were readily separated by fractional distillation and were free of halogenated material (cf. McRae *et al.* (10)). On the basis of refractive index and infrared spectra of the various fractions (see Table V) it was estimated that the yield of *trans*-, or lower-boiling, oxide is 63% and that of the *cis*-, or higher-boiling, oxide is 19%. Thus, the percentages of *trans*- and *cis*-oxide in the mixture are 77% and 23% respectively, suggesting the same percentage composition for the 1-methoxycyclohexene-2 bromohydrin mixture. In a similar manner the stereoisomeric *dl*-1-ethoxy-2,3-epoxycyclohexanes (VII and VIII; R = C_2H_5) were obtained in 88% yield. The yield of *trans*-oxide was estimated to be 70.5% and that of the *cis*-oxide 17.5%, giving a distribution of 80% *trans*- and 20% *cis*-oxide in the mixture. It is evident from Table IV that fractionation of the 1-ethoxy-2,3-epoxycyclohexanes was not as clean cut as with the corresponding methoxy compounds. This result was unexpected in view of the difference in boiling points of the isomers and the high reflux ratio used.

The spectra of the 1-methoxy- and 1-ethoxy-2,3-epoxycyclohexanes are shown in Figs. 1 to 4. These substances give a strong band at 1100 cm^{-1} characteristic of the unsymmetrical C—O—C stretching vibration in aliphatic ethers (16). Absorption due to the symmetrical ring stretching vibration of the oxirane ring was observed in the characteristic 1250 cm^{-1} region (16). In each case, the *trans*-isomer showed a medium intensity band at 1245 cm^{-1} and the *cis*-isomer showed a similar band at 1255 cm^{-1}. It is possible to use the bands at 1245 and 1255 cm^{-1} as criteria of purity of the oxides but the change in intensity of these bands is not sufficiently great to permit accurate quantitative



FIGS. 1–4. Infrared spectra of the 1-alkoxy-2,3-epoxycyclohexanes.

estimation of the compositions of mixtures—the refractive index gives a more sensitive method. However, there are a number of bands in the region 690–1380 cm^{-1} which show great differences in intensity as the composition of mixtures of the *trans*- and *cis*-oxides change, some of which could undoubtedly be used for quantitative estimation by means of a suitable calibration curve. The *trans*-oxides show prominent characteristic bands at 775, 795, 800, 825, 980, 1200, and 1380 cm^{-1}, whereas the *cis*-oxides show prominent characteristic bands at 690, 755, 790, 845, 865, and 1325 cm^{-1}. The forerun of each oxide contained a trace of carbonyl impurity as shown by the appearance of a weak band at 1675 cm^{-1}. This carbonyl impurity could be due to the presence of a trace of *cis*-bromohydrin in the predominantly *trans*-oriented bromohydrin mixture (17), since the action of alkali on the former would lead to ketone rather than epoxide (18, 19).

Ammonolysis of *dl*-1β-methoxy-2α,3α-epoxycyclohexane* (VII; R = CH_3) with aqueous ethanolic ammonia by Hawkins and Bannard's method (12) gave *dl*-1α-methoxy-2β-hydroxy-3α-aminocyclohexane (IX; R = CH_3), m.p. 107–108°, in 84% yield, uncontaminated with its isomer X (R = CH_3), as shown by paper chromatography. In a similar manner, ammonolysis of *dl*-1α-methoxy-2α,3α-epoxycyclohexane (VIII; R = CH_3) produced *dl*-1α-methoxy-2α-hydroxy-3β-aminocyclohexane (X; R = CH_3), m.p. 94°, in 75% yield, uncontaminated with its isomer IX (R = CH_3). The two 1-methoxy-2-hydroxy-3-aminocyclohexanes (IX and X; R = CH_3) were shown to be distinctly different by comparison of their infrared spectra, paper chromatographic behavior (see Table VI), a mixed melting-point determination (m.p. 72–92°), and preparation of their hydrobromides, and N-acetyl, N-*p*-nitrobenzoyl, and N-phenylthiourea derivatives listed in Table I.

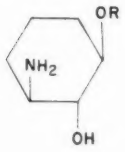
TABLE I

DERIVATIVES OF THE 1-ALKOXY-2-HYDROXY-3-AMINOCYCLOHEXANES

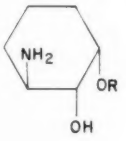
Compound	Derivative	% Yield	M.p. (° C)	Analysis % C Calc.	% C Found	% H Calc.	% H Found	% N Calc.	% N Found	% Br Calc.	% Br Found	% S Calc.	% S Found
dl-1α-Methoxy-2β-hydroxy-3α-aminocyclohexane	Hydrobromide	80	206 –207	37.18	37.20	7.14	7.10	6.20	6.30	35.34	35.72		
	N-Acetyl	82	115.5–116.5	57.75	57.90	9.16	9.04	7.48	7.27				
	N-*p*-Nitrobenzoyl	85	178 –179.5	57.14	57.21	6.16	5.87	9.52	9.57				
	N-Phenylthiourea	77	135 –136	59.99	60.28	7.19	7.24	10.00	10.18			11.44	11.38
dl-1α-Methoxy-2α-hydroxy-3β-aminocyclohexane	Hydrobromide	81	203 –204	37.18	37.30	7.14	7.17	6.20	6.44	35.34	35.44		
	N-Acetyl	77	154.5–155	57.75	58.00	9.16	9.32	7.48	7.41				
	N-*p*-Nitrobenzoyl	85	238.5–239	57.14	57.14	6.16	6.28	9.52	9.63				
	N-Phenylthiourea	62	155 –156	59.99	60.06	7.19	7.09	10.00	10.12			11.44	11.60
dl-1α-Ethoxy-2β-hydroxy-3α-aminocyclohexane	Hydrobromide	76	194.5–196	40.00	40.18	7.55	7.59	5.83	6.04	33.27	33.18		
	N-Acetyl	77	124	59.69	59.79	9.52	9.58	6.96	6.74				
	N-*p*-Nitrobenzoyl[a]	87	203 –204	58.45	58.34	6.54	6.43	9.09	9.07				
	N-Phenylthiourea	70	133 –134	61.17	61.28	7.53	7.67	9.52	9.55			10.89	11.07
dl-1α-Ethoxy-2α-hydroxy-3β-aminocyclohexane	Hydrobromide	79	179 –180	40.00	40.22	7.55	7.59	5.83	6.08	33.27	33.14		
	N-Acetyl	82	129 –129.5	59.69	59.77	9.52	9.55	6.96	6.66				
	N-*p*-Nitrobenzoyl	84	215.5–216	58.45	58.34	6.54	6.52	9.09	9.06				
	N-Phenylthiourea	76	143 –144	61.17	61.26	7.53	7.54	9.52	9.70			10.89	10.97

[a]McCasland *et al.* (4) report m.p. 201–203°.

**The system of nomenclature used to describe the configurations of the 1-alkoxy-2,3-epoxycyclohexanes and compounds obtained on scission of the oxirane ring conforms to that used by Lemieux, Kullnig, and Moir (13).*

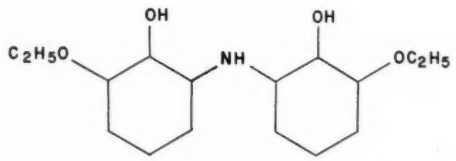


(IX)



(X)

Ammonolysis of *dl*-1β-ethoxy-2α,3α-epoxycyclohexane (VII; R = C_2H_5) gave *dl*-1α-ethoxy-2β-hydroxy-3α-aminocyclohexane (IX; R = C_2H_5), m.p. 134.5–135.5°, in 77% yield, uncontaminated with its isomer X (R = C_2H_5). In one experiment in which an ammonia/oxide ratio of less than 20:1 was used, a small amount of the secondary amine α,α-bis-(2β-hydroxy-3α-ethoxycyclohexyl)amine (XI) was obtained and isolated as the hydrobromide, m.p. 313–314° (cf. Hawkins and Bannard (12)). Ammonolysis of *dl*-1α-ethoxy-2α,3α-epoxycyclohexane (VIII; R = C_2H_5) furnished *dl*-1α-ethoxy-2α-hydroxy-3β-aminocyclohexane (X; R = C_2H_5), m.p. 133–134°, in 89% yield, uncontaminated with its isomer IX (R = C_2H_5). The two 1-ethoxy-2-hydroxy-3-aminocyclohexanes (IX and X; R = C_2H_5) were shown to differ from one another by comparison of infrared spectra, paper chromatographic behavior (see Table VI), a mixed melting-point determination (m.p. 116–118°), and preparation of their hydrobromides and N-acetyl, N-*p*-nitrobenzoyl, and N-phenylthiourea derivatives given in Table I.



(XI)

It is evident from the melting points of the N-*p*-nitrobenzoyl derivatives of the *dl*-1-ethoxy-2-hydroxy-3-aminocyclohexanes (Table I) that McCasland *et al.* (4) obtained *dl*-1α-ethoxy-2β-hydroxy-3α-aminocyclohexane (IX; R = C_2H_5). This result was anticipated in view of the fact that the *trans*-oxide greatly predominates in the mixture of stereoisomeric oxides resulting from the action of alkali on the 1-ethoxycyclohexene-2 bromohydrins, implying that a similar situation would prevail in the case of the corresponding chlorohydrins. A similar result (i.e. predomination of *trans*-oxide) would also be expected when the oxide is prepared by peracid oxidation of 1-methoxycyclohexene-2 (1, 2, 3, 4,), since Henbest and Wilson (20, 21) have found that peracid oxidation of cyclic allylic esters or ethers yields predominantly the *trans*-oxide. It thus seems certain that Mousseron *et al.* (1, 2, 3) obtained the same compound as McCasland *et al.* (4) but in a less pure condition.

Ether cleavage of *dl*-1α-methoxy-2β-hydroxy-3α-aminocyclohexane or *dl*-1α-ethoxy-2β-hydroxy-3α-aminocyclohexane (IX; R = CH_3 or C_2H_5) with 47% hydrobromic acid gave *dl*-3α-amino-1α,2β-cyclohexanediol hydrobromide, m.p. 168–169°, in 90% yield,

which was converted to the free base I, m.p. 151°, in 87% yield. In a similar manner, ether cleavage of *dl*-1α-methoxy-2α-hydroxy-3β-aminocyclohexane or *dl*-1α-ethoxy-2α-hydroxy-3β-aminocyclohexane (X; R = CH_3 or C_2H_5) gave *dl*-3β-amino-1α,2α-cyclohexanediol hydrobromide, m.p. 165.5–167°, in 70% yield, which was converted to the free base II, m.p. 104–105°, in 95% yield. The two aminediols were shown to be quite different by a mixed melting-point determination with their hydrobromides (m.p. 145–150°), comparison of their infrared spectra and paper chromatographic behavior (see Table VI), and preparation of the N-*p*-nitrobenzoyl, N-phenylthiourea, and triacetyl derivatives listed in Table II.

TABLE II

DERIVATIVES OF THE 3-AMINO-1,2-CYCLOHEXANEDIOLS

Compound	Derivative	% Yield	M.p. (° C)	Analysis							
				% C		% H		% N		% S	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
dl-3α-Amino-1α,2β-cyclohexanediol	N-*p*-Nitrobenzoyl	74	185–187	55.71	55.39	5.75	5.77	10.00	9.89		
	N-Phenylthiourea*	98	115–117	57.65	57.06	7.74	7.70	8.97	8.81	10.26	10.31
	Triacetyl	80	193–194	56.02	56.02	7.44	7.39	5.44	5.57		
dl-3β-Amino-1α,2α-cyclohexanediol	N-*p*-Nitrobenzoyl	65	195–197	55.71	55.57	5.75	5.85	10.00	9.74		
	N-Phenylthiourea	80	151–152.5	58.61	58.66	6.81	6.86	10.52	10.84	12.03	11.88
	Triacetyl	59	148–149.5	56.02	55.80	7.44	7.56	5.44	5.22		

*Contains 1 molecule of ethanol of crystallization.

The data presented above establish the stereochemical identity of the 1-alkoxy-2-hydroxy-3-aminocyclohexanes (IX; R = CH_3 or C_2H_5) resulting from ammonolysis of the α- or lower-boiling 1-alkoxy-2,3-epoxycyclohexanes (VII; R = CH_3 or C_2H_5) and necessarily also show the stereochemical equivalence of the two oxides. Similarly the stereochemical identity of the 1-alkoxy-2-hydroxy-3-aminocyclohexanes (X; R = CH_3 or C_2H_5) resulting from ammonolysis of the β- or higher-boiling 1-alkoxy-2,3-epoxycyclohexanes (VIII; R = CH_3 or C_2H_5) has also been demonstrated and the stereochemical equivalence of the two oxides follows. Furthermore, it has been clearly shown that the α- and β-oxides differ from one another since they lead to distinctly different aminocyclohexanediols. The aminediols were shown to be 3-amino-1,2-cyclohexanediols, since the N-*p*-nitrobenzoyl derivative in each case rapidly consumed 1 mole of periodate at 25° (22). However, reaction was so rapid at this temperature that the relative rates of oxidation of the two isomers could not be observed with sufficient accuracy to permit stereochemical assignment to the diols. Repetition of the oxidation with sodium metaperiodate at 3°, however, gave the results shown in Fig. 5. Comparison of the $t_{\frac{1}{2}}$ values makes it clear that the diol group in the aminediol resulting from ammonolysis of the β-oxides must be assigned the *cis*-configuration II and the diol group in the aminediol from ammonolysis of the α-oxides must possess the *trans*-configuration I, since the N-*p*-nitrobenzoyl derivative of the former is oxidized 7.5 times more rapidly than that of the latter (23, 24, 25).

The N-phenylthiourea derivatives of the aminediols were prepared in the expectation that determination of relative rates of cleavage of the isomers with periodate would lead to confirmation of the structures assigned above. However, the periodate cleavage of these derivatives proved abnormal in that even the N-phenylthiourea derivative of

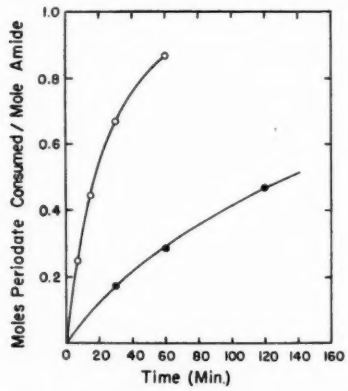


FIG. 5. Rate of periodate oxidation of the 3-*p*-nitrobenzamido-1,2-cyclohexanediols.
● 3α-*p*-Nitrobenzamido-1α,2β-cyclohexanediol
○ 3β-*p*-Nitrobenzamido-1α,2α-cyclohexanediol

trans-2-aminocyclohexanol reacted rapidly with periodate. Thus, these derivatives cannot be used to protect an amine function during diol scission with periodate.

Ionophoretic migration of *cis*-1,2-diols in borate buffer is generally considered to be associated with formation of ionized chelated complexes (25, 26) and has been used to deduce the structure of cyclitols (27). The ionophoretic mobilities of the N-*p*-nitrobenzoyl and N-phenylthiourea derivatives of the aminediols I and II in 0.1 *M* sodium tetraborate were determined. In each case (see Table VII) the derivative arising from the β- or higher-boiling 1-alkoxy-2,3-epoxycyclohexanes exhibited ionophoretic mobility, while the derivative obtained from the α- or lower-boiling 1-alkoxy-2,3-epoxycyclohexanes did not migrate, thus leading to the conclusion that derivatives obtained by oxide ring scission of the former compounds contain a *cis*-1,2-diol group (I), whereas derivatives obtained similarly from the latter compounds contain a *trans*-1,2-diol group (II). This result confirms the structural assignment made on the basis of relative rates of periodate cleavage of the aminediol N-*p*-nitrobenzoyl derivatives.

It is assumed throughout that opening of the oxirane ring under the basic conditions used is accompanied by Walden inversion at the reactive carbon atom (i.e. C_3) (4, 5, 6, 14, 28, 29), and that ether cleavage is not attended by Walden inversion (see Gogek *et al.* (14) and references there cited, also Lemieux, Kullnig, and Moir (13)). Assignment of structure I to the *trans*-diol leads to structure IX (R = CH_3 or C_2H_5) for the 3-amino-1-alkoxy-2-hydroxycyclohexanes derived from the α-oxides and hence to the *trans* structure VII (R = CH_3 or C_2H_5) for the latter, in agreement with the conclusion reached by Lemieux, Kullnig, and Moir (13) in the case of the α-methoxy oxide (VII; R = CH_3). In a similar manner, assignment of structure II to the *cis*-diol leads to structure X (R = CH_3 or C_2H_5) for the 3-amino-1-alkoxy-2-hydroxycyclohexanes derived from the β-oxides and hence to the *cis* structure VIII (R = CH_3 or C_2H_5) for the latter.

Lemieux, Kullnig, and Moir (13) have pointed out that both 1-methoxy-2,3-epoxycyclohexanes (VII and VIII; R = CH_3) show a preference for attack at position 3 by nucleophilic reagents and suggest that such preference is probably an electronic effect of the presence of the electronegative alkoxyl group, rather than a steric effect. This suggestion receives support from the results reported above on ammonolysis of the 1-methoxy- and 1-ethoxy-2,3-epoxycyclohexanes (VII and VIII; R = CH_3 or C_2H_5).

EXPERIMENTAL*†

trans-1,2-Dibromocyclohexane

trans-1,2-Dibromocyclohexane was prepared by the method of Snyder and Brooks (30).

1-Methoxycyclohexene-2

1-Methoxycyclohexene-2 was prepared by the method of Gogek *et al.* (14), with the method of isolation modified as follows. After the solution of *trans*-1,2-dibromocyclohexane (3.88 g, 1.60 moles), sodium (90.0 g, 3.9 g-atoms), and absolute methanol (1100 ml) had been heated under reflux for 10 hours, the precipitated sodium bromide was collected by suction filtration and washed with anhydrous ether (6×50 ml). The filtrate and washings were distilled on the steam bath first at atmospheric pressure and finally at 25–30 mm pressure until a semisolid mushy residue remained. The residue was treated with water (200 ml) and the solution was extracted with ether (3×50 ml). The extracts were combined with the earlier distillates and the solution was fractionated slowly at atmospheric pressure using a 20-inch vacuum-jacketed Stedman column, yielding 134 g (74.8%) of 1-methoxycyclohexene-2 as a colorless mobile fragrant liquid, b.p. 138–139°, n_D^{25} 1.4513–1.4518. Gogek *et al.* (14) report a 60% yield of substance, b.p. 139°. Berlande (31) has reported n_D^{20} 1.4530.

1-Ethoxycyclohexene-2

1-Ethoxycyclohexene-2 was prepared by the same method as described above for 1-methoxycyclohexene-2. Yield, 58.5%, b.p. 153–154°, n_D^{25} 1.4490. Berlande (31) has reported b.p. 156°, and n_D^{20} 1.4585. Fenton (11) reported b.p. 153–153.5°.

1-Ethoxycyclohexene-2 Chlorohydrin

1-Ethoxycyclohexene-2 chlorohydrin was prepared by the method of Fenton (11) using monochlorourea as the source of hypochlorous acid. From 378 g (3.0 mole) of 1-ethoxycyclohexene-2, 358 g of colorless to pale yellow liquid, b.p. 108–113° at 11–13 mm pressure, n_D^{25} 1.4784–1.4794, was obtained. Fenton (11) reported b.p. 105–120° at 20 mm pressure and McCasland *et al.* (4) reported b.p. 110–117° at 12 mm. Refractionation at 1–2 mm pressure of 770 g of chlorohydrin prepared by the above method gave the fractions indicated in Table III.

TABLE III

FRACTIONATION OF 1-ETHOXYCYCLOHEXENE-2 CHLOROHYDRIN

Fraction No.	B.p. (° C)	Weight (g)	Refractive index n_D^{25}	Analysis[a]		
				% C	% H	% Cl
1	76 –77.5	249	1.4788	51.48	8.17	26.50
2	77.5–78	88	1.4789	52.02	7.98	25.24
3	78 –79.5	84	1.4792	52.43	8.11	24.56
4	79.5–81	92	1.4795	52.88	8.22	23.09
5	79.5–80	80	1.4798	53.23	8.48	22.15
6	80 –81	46	1.4798	53.35	8.46	21.23
7	83 –89	77	1.4800	52.38	8.21	21.10
8	Pot residue	34	1.4816	50.76	7.77	24.24

[a]Calc. for $C_8H_{15}O_2Cl$: C, 53.78; H, 8.46; Cl, 19.85%.
Calc. for $C_8H_{14}OCl_2$: C, 48.75; H, 7.16; Cl, 35.97%.

1-Ethoxycyclohexene-2 Bromohydrin

N-Bromosuccinimide (178 g, 1.00 mole), 1-ethoxycyclohexene-2 (132 g, 1.05 mole),

**All melting points and boiling points are uncorrected.*
†Microanalyses by Micro-Tech Labs., Skokie, Ill., and J. G. Helie, of these laboratories.

and water (500 ml) were mixed at 25° in a 1-liter three-necked flask equipped with a "trubore" stirrer and thermometer (12). Stirring was continued until the N-bromosuccinimide dissolved (20 minutes) and a heavy colorless layer of bromohydrin separated, during which time the temperature rose to 75°. The two-phase system was allowed to cool to room temperature, the bromohydrin layer was separated, and the aqueous phase was extracted with ether (2×100 ml). The extracts and bromohydrin were combined and the ether removed by distillation *in vacuo*. The residue was kept overnight at 4°, after which the precipitated succinimide was removed by filtration. The filtrate was fractionated *in vacuo* yielding 190 g (85.2%) of 1-ethoxycyclohexene-2 bromohydrin as a colorless oil, b.p. 87.5–91.5° at 0.3 mm, n_D^{25} 1.5018–1.5025. Calc. for $C_8H_{15}O_2Br$: C, 43.07; H, 6.78; Br, 35.82%. Found: C, 42.95; H, 6.82; Br, 35.82%.

1-Methoxycyclohexene-2 Bromohydrin

1-Methoxycyclohexene-2 bromohydrin was prepared in exactly the same manner as described for 1-ethoxycyclohexene-2 bromohydrin. Yield, 161 g (77.0%) of colorless oil, b.p. 94–97° at 1 mm, n_D^{25} 1.5120–1.5131. Calc. for $C_7H_{13}O_2Br$: C, 40.22; H, 6.27; Br, 38.22%. Found: C, 40.08; H, 6.35; Br, 37.98%.

dl-1β-Ethoxy-2α,3α-epoxycyclohexane and dl-1-α-Ethoxy-2α,3α-epoxycyclohexane (VII and VIII; R = C_2H_5)

1-Ethoxycyclohexene-2 bromohydrin (234 g, 1.05 mole) was treated with aqueous sodium hydroxide (120 g, 2.94 moles, 300 ml) at 25° with mechanical stirring. The temperature rose to 35° and the lower bromohydrin layer was replaced by a supernatant layer of colorless oxide. The mixture was heated at 75° for 1 hour with continuous stirring, and cooled to room temperature; the oxide layer was then separated and the aqueous phase extracted with ether (3×100 ml). The combined oxide and ether extracts were dried over anhydrous magnesium sulphate, after which the ether was removed *in vacuo*. The colorless residue was fractionated at 10 mm pressure using a Podbielniak Whirling Heli-Band column, employing diphenylmethane as "chaser" during the final stage of fractionation, giving the results shown in Table IV.

TABLE IV

FRACTIONATION OF 1-ETHOXY-2,3-EPOXYCYCLOHEXANES

Fraction No.	B.p. (°C)	Refractive index n_D^{25}	Weight (g)	Analysis*	
				% C	% H
1	55.5–56.0	1.4484	84.2	67.52	10.01
2	56.0–56.5	1.4491	21.6	67.80	10.14
3	56.5–64.5	1.4520	2.3	67.63	9.91
4	64.5–65.5	1.4554	23.0	67.81	10.11
			131		

*Calc. for $C_8H_{14}O_2$: C, 67.58; H, 9.92%.

From Table IV it is clear that the 1-ethoxy-2,3-epoxycyclohexanes were obtained in 88.0% yield. Fraction 1 is pure *trans*-oxide, since the infrared spectrum of this compound showed the characteristic oxirane band at 1245 cm^{-1}, and fraction 4 is pure *cis*-oxide, since its infrared spectrum showed the characteristic oxirane band at 1255 cm^{-1}. Fractions 2 and 3 are mixtures of the two oxides, since both the above-mentioned bands were present in the infrared spectra. Mixtures of the pure oxides gave a linear relationship between refractive index and percentage composition and the yields of the two

oxides were estimated. The yield of *trans*-oxide is 105 g (70.4%) and that of *cis*-oxide is 26.3 g (17.6%), i.e. the mixture consists of 80% *trans*-oxide and 20% *cis*-oxide. Fenton (11) reported b.p. 82–84° at 20 mm for *trans*-oxide and 97–100° at 20 mm for *cis*-oxide. McCasland *et al.* (4) gave b.p. 79–82° at 15–16 mm and n_D^{25} 1.4530 for the oxide mixture resulting from peracid oxidation of 1-ethoxycyclohexene-2, and Mousseron *et al.* (3) gave b.p. 77–78° at 12 mm and n_D^{25} 1.4493 for a similar product.

dl-1β-Methoxy-2α,3α-epoxycyclohexane and dl-1α-Methoxy-2α,3α-epoxycyclohexane (VII and VIII; R = CH_3)

1-Methoxycyclohexene-2 bromohydrin (146 g, 0.70 mole) was treated with aqueous sodium hydroxide (84.0 g, 2.04 mole, 200 ml), as described for the preparation of the corresponding ethoxy compounds, yielding, after subsequent manipulation as described above, the fractions shown in Table V.

TABLE V

FRACTIONATION OF 1-METHOXY-2,3-EPOXYCYCLOHEXANES

Fraction No.	B.p. (° C)	Refractive index n_D^{25}	Weight (g)	Analysis*	
				% C	% H
1	54–55	1.4512	55.0	65.69	9.52
2	55–65	1.4520	0.7	65.82	9.57
3	65–69	1.4545	1.9	65.80	9.66
4	69–71	1.4585	17.4	65.71	9.56
			75		

*Calc. for $C_7H_{12}O_2$: C, 65.58; H, 9.44%.

From Table V it is evident that the yield of 1-methoxy-2,3-epoxycyclohexane mixture is 83.8%. Fraction 1 is pure *trans*-oxide and fraction 4 is pure *cis*-oxide, while fractions 2 and 3 are mixtures (infrared spectra). As in the case of the corresponding ethoxy compounds the composition of mixtures was estimated on the basis of refractive index. The yield of *trans*-oxide is thus 56.5 g (63.2%) and that of *cis*-oxide 17.4 g (19.4%), i.e. the mixture consists of approximately 77% *trans*-oxide and 23% *cis*-oxide. McRae *et al.* (10) have reported b.p. 67–69° at 15 mm and n_D^{20} 1.4532 for the *trans*-oxide and b.p. 75–85° at 12 mm and n_D^{20} 1.4603 for the *cis*-oxide.

dl-1α-Methoxy-2β-hydroxy-3α-aminocyclohexane (IX; R = CH_3)

dl-1β-Methoxy-2α,3α-epoxycyclohexane (12.8 g, 0.100 mole) was heated for 1 hour at 100° in a stainless-steel bomb with 28% aqueous ammonia (135 ml, 2 moles) and absolute ethanol (60 ml) (12). The solution was evaporated to dryness *in vacuo* and the resultant buff-colored amine was sublimed at 110–120° at 1 mm, yielding 12.1 g (83.5%) of colorless *dl*-1α-methoxy-2β-hydroxy-3α-aminocyclohexane, m.p. 107–108°. Calc. for $C_7H_{15}O_2N$: C, 57.90; H, 10.41; N, 9.65%. Found: C, 57.52; H, 10.39; N, 9.58%.

dl-1α-Methoxy-2α-hydroxy-3β-aminocyclohexane (X; R = CH_3)

dl-1α-Methoxy-2α,3α-epoxycyclohexane (15.0 g, 0.117 mole) was ammonolyzed with aqueous ethanolic ammonia under the conditions described for 1β-methoxy-2α,3α-epoxycyclohexane, yielding 12.8 g (75.3%) of *dl*-1α-methoxy-2α-hydroxy-3β-aminocyclohexane as colorless feathery needles, m.p. 94°, after recrystallization from ethanol–ether. Calc. for $C_7H_{15}O_2N$: C, 57.90; H, 10.41; N, 9.65%. Found: C, 57.47; H, 10.39; N, 9.58%.

dl-1α-Ethoxy-2β-hydroxy-3α-aminocyclohexane (IX; R = C_2H_5)

dl-1β-Ethoxy-2α,3α-epoxycyclohexane (31.1 g, 0.219 mole) was ammonolyzed with aqueous ethanolic ammonia under the conditions described for *dl*-1β-methoxy-2α,3α-epoxycyclohexane, yielding 26.8 g (77.0%) of *dl*-1α-ethoxy-2β-hydroxy-3α-aminocyclohexane as colorless platelets, m.p. 134.5–135.5°, after recrystallization from ethanol–ether. McCasland *et al.* (4) report m.p. 132–134° for this compound. Calc. for $C_8H_{17}O_2N$: C, 60.35; H, 10.76; N, 8.80%. Found: C, 60.67; H, 10.93; N, 8.72%.

In one experiment in which the ammonia–oxide ratio was less than 20:1 a small amount of α,α-bis-(2β-hydroxy-3α-ethoxycyclohexyl)amine was obtained, and isolated as the hydrobromide, m.p. 313–314°. Calc. for $C_{16}H_{32}O_4NBr$; C, 50.27; H, 8.44; N, 3.66; Br, 20.9%. Found: C, 50.36; H, 8.47; N, 4.12; Br, 20.93%.

dl-1α-Ethoxy-2α-hydroxy-3β-aminocyclohexane (X; R = C_2H_5)

dl-1α-Ethoxy-2α,3α-epoxycyclohexane (16.1 g, 0.113 mole) was ammonolyzed with aqueous ethanolic ammonia under the conditions described for *dl*-1β-methoxy-2α,3α-epoxycyclohexane, yielding 16.0 g (88.8%) of *dl*-1α-ethoxy-2α-hydroxy-3β-aminocyclohexane as fine colorless needles, m.p. 133–134°, after recrystallization from ethanol–ether. Calc. for $C_8H_{17}O_2N$: C, 60.35; H, 10.76; N, 8.80%. Found: C, 60.51; H, 10.83; N, 8.73%.

Derivatives of the dl-1-Alkoxy-2-hydroxy-3-aminocyclohexanes

The *dl*-1-alkoxy-2-hydroxy-3-aminocyclohexanes reported above were characterized as their hydrobromides and N-acetyl, N-*p*-nitrobenzoyl, and N-phenylthiourea derivatives. The hydrobromides and N-phenylthiourea derivatives were prepared by standard methods. The N-*p*-nitrobenzoyl derivatives were prepared by Leffler and Adams' procedure (32). The N-acetyl derivatives were obtained by treating the alkoxyaminocyclohexanols with a 10% excess of acetic anhydride at room temperature, followed by evaporation to dryness *in vacuo*, and recrystallization from ethanol–ether. Yields, melting points, and analytical data for the derivatives are given in Table I.

dl-3α-Amino-1α,2β-cyclohexanediol Hydrobromide

(*a*) *From dl-1α-Ethoxy-2β-hydroxy-3α-aminocyclohexane* (IX; R = C_2H_5)

dl-1α-Ethoxy-2β-hydroxy-3α-aminocyclohexane (60.0 g, 0.377 mole) was heated under reflux for 1½ hours with 48% hydrobromic acid (230 ml, 2.0 moles). Most of the excess acid was removed by distillation *in vacuo* but no attempt was made to distill to dryness (cf. McCasland *et al.* (4)). The residue was treated with ether (300 ml) and ethanol (75 ml) and evaporated *in vacuo* to small volume. This operation was repeated, after which 300 ml of ether was added, followed by just sufficient ethanol to produce a clear solution. When the solution was allowed to stand at 4°, *dl*-3α-amino-1α,2β-cyclohexanediol hydrobromide separated as colorless to light-grey rosettes. Yield, 73.1 g (91.4%), m.p. 168–169°. McCasland *et al.* (4) report m.p. 167–168°. Calc. for $C_6H_{14}O_2NBr$: C, 33.98; H, 6.65; N, 6.61; Br, 37.68%. Found: C, 33.89; H, 6.71; N, 6.66; Br, 37.64%.

(*b*) *From dl-1α-Methoxy-2β-hydroxy-3α-aminocyclohexane* (IX; R = CH_3)

dl-1α-Methoxy-2β-hydroxy-3α-aminocyclohexane (35.0 g, 0.241 mole) was subjected to ether cleavage under the conditions described above. Crystallization of the product from ethanol–ether furnished 46.3 g (90.5%) of *dl*-3α-amino-1α,2β-cyclohexanediol hydrobromide as colorless to light-grey rosettes, m.p. 167.5–169°. Admixture of this substance with that obtained in (*a*) above did not depress the melting point. The two samples gave identical infrared spectra, and moved with the same speed in paper chromatograms (R_F 0.40, see Table VI).

dl-3α-Amino-1α,2β-cyclohexanediol (I)

dl-3α-Amino-1α,2β-cyclohexanediol hydrobromide (60.0 g, 0.283 mole) was dissolved in a solution of sodium hydroxide (11.8 g, 0.286 mole in 100 ml water). Evaporation to dryness *in vacuo* gave a light-tan crystalline residue, which was sublimed at 140° at 0.5 mm to free it from inorganic material. Recrystallization of the sublimate from absolute ethanol yielded 32.4 g (87.4%) of *dl*-3α-amino-1α,2β-cyclohexanediol, m.p. 151°, as colorless prisms. Calc. for $C_6H_{13}O_2N$: C, 54.93; H, 9.99; N, 10.68%. Found: C, 55.05; H, 10.11; N, 10.71%.

dl-3β-Amino-1α,2α-cyclohexanediol Hydrobromide

(*a*) *From dl-1α-Ethoxy-2α-hydroxy-3β-aminocyclohexane* (X; R = C_2H_5)

dl-1α-Ethoxy-2α-hydroxy-3β-aminocyclohexane (14.0 g, 0.88 mole) was subjected to ether cleavage under the conditions described for its isomer. Crystallization from ethanol–ether gave 13.0 g (69.8%) of *dl*-3β-amino-1α,2α-cyclohexanediol hydrobomide as colorless rosettes, m.p. 165.5–167°. Calc. for $C_6H_{14}O_2NBr$: C, 33.98; H, 6.65; N, 6.61; Br, 37.68%. Found: C, 34.31; H, 6.86; N, 6.79; Br, 37.36%.

(*b*) *From dl-1α-Methoxy-2α-hydroxy-3β-aminocyclohexane* (X; R = CH_3)

dl-1α-Methoxy-2α-hydroxy-3β-aminocyclohexane (5.30 g, 0.0365 mole) was subjected to ether cleavage under the conditions described for *dl*-1α-ethoxy-2β-hydroxy-3α-amino-cyclohexane. Crystallization from ethanol–ether gave 5.40 g (69.8%) of colorless rosettes, m.p. 165.5–167°. Admixture of this substance with the compound isolated from (*a*) above caused no depression in melting point. The two samples likewise gave identical infrared spectra and moved with the same speed in paper chromatograms (R_F 0.43, see Table VI).

dl-3β-Amino-1α,2α-cyclohexanediol (II)

dl-3β-Amino-1α,2α-cyclohexanediol hydrobromide (14.0 g, 0.066 mole) was converted to the free base by passing a 5% aqueous solution through Amberlite IRA-400 resin in the hydroxide form. Evaporation to dryness *in vacuo* followed by recrystallization from benezene gave 5.90 g (95.3%) of *dl*-3β-amino-1α,2α-cyclohexanediol, m.p. 104–105°, as colorless prisms. Calc. for $C_6H_{13}O_2N$: C, 54.93; H, 9.99; N, 10.68%. Found: C, 55.02; H, 10.00; N, 10.77%.

Derivatives of the dl-3-Amino-1,2-cyclohexanediols

The *dl*-3-amino-1,2-cyclohexanediols were characterized as their N-*p*-nitrobenzoyl, N-phenylthiourea, and triacetyl derivatives. The same methods were used as in preparation of derivatives of the 1-alkoxy-2-hydroxy-3-aminocyclohexanes, except that in preparation of the triacetyl compounds, a 10-fold excess of acetic anhydride was used. Yields, melting points, and analytical data for the derivatives are given in Table II.

N-Phenylthiourea Derivative of dl-trans-2-Aminocyclohexanol

The same method was used as for preparation of the N-phenylthiourea derivatives of the *dl*-1-alkoxy-2-hydroxy-3-aminocyclohexanes. Yield, 93%, m.p. 144.5°. Calc. for $C_{13}H_{18}N_2SO$: C, 62.37; H, 7.25; N, 11.19; S, 12.80%. Found: C, 62.09; H, 7.22; N, 11.29; S, 12.69%.

Paper Chromatography of the 3-Amino-1,2-cyclohexanediols and Derivatives

For paper chromatography 2% solutions of the compounds in water, ethanol, or acetone were applied to unwashed Whatman No. 1 paper (7.5 λ spots). The chromatograms were developed overnight in a glass tank by the descending technique using *n*-butanol – acetic acid – water (25:6:25) as developer. The air-dried chromatograms were sprayed with bromcresol green for detection of the free amines and with ammoniacal

TABLE VI

R_F VALUES OF 3-AMINO-1,2-CYCLOHEXANEDIOL DERIVATIVES IN *n*-BUTANOL – ACETIC ACID – WATER (25:6:25)

Compound	R_F
1α-Methoxy-2β-hydroxy-3α-aminocyclohexane	0.51
1α-Methoxy-2α-hydroxy-3β-aminocyclohexane	0.55
1α-Ethoxy-2β-hydroxy-3α-aminocyclohexane	0.60
1α-Ethoxy-2α-hydroxy-3β-aminocyclohexane	0.66
α,α-bis-(2β-Hydroxy-3α-ethoxycyclohexyl)amine	0.74
3α-Amino-1α,2β-cyclohexanediol	0.40
3β-Amino-1α,2α-cyclohexanediol	0.43
3α-N-*p*-Nitrobenzamido-1α,2β-cyclohexanediol	0.87
3β-N-*p*-Nitrobenzamido-1α,2α-cyclohexanediol	0.88
2β-Amino-1α-cyclohexanol	0.59

silver nitrate (33) for detection of the N-*p*-nitrobenzoyl derivatives of the aminediols. R_F values are given in Table VI.

Periodate Oxidation of dl-3α-p-Nitrobenzamido-2β,3α-cyclohexanediol and dl-3β-p-Nitrobenzamido-2α,3α-cyclohexanediol

(*a*) *At 25° C*

A 40-mg sample of each aminediol *p*-nitrobenzoyl derivative was treated with 0.1053 *N* paraperiodic acid (20.00 ml) at 25°. Iodometric titrations with sodium arsenite (22) revealed that 0.95 mole of paraperiodic acid was consumed per mole of *cis*-diol derivative in 60 minutes and 0.96 mole of paraperiodic acid was consumed per mole of *trans*-diol derivative in 90 minutes.

(*b*) *At 3° C*

A 20-mg sample of aminediol derivative was dissolved in 50 ml of water at room temperature and the solution was cooled to 3°. At time zero, sodium metaperiodate (10.00 ml, 0.0300 *N*) at 3° was pipetted into the solution, which was stirred constantly in a constant temperature bath at 3°±0.1°. The reaction was allowed to proceed for a specified length of time, after which further reaction was stopped by addition of sodium bicarbonate (2 g, A.R.), sodium arsenite (25.00 ml, 0.0200 *N*), and potassium iodide solution (1 ml, 20%). The consumption of periodate was determined by back-titration with 0.0100 *N* iodine (22) and the quantity of aminediol derivative oxidized calculated. Results are shown in Fig. 5.

Electrophoresis of 3-Amino-1,2-cyclohexanediol Derivatives on Glass Paper

The aminediol derivatives (1% solution in acetone) were spotted on 63×380 mm strips of glass fiber paper (H. Reeve Angel and Co., Inc.) together with D-glucose and 2,3,4,6-tetramethyl-D-glucose as reference compounds. The strips were placed in a water-cooled closed strip-type apparatus (E.C. Apparatus Co., Model No. 401) con-

TABLE VII

M_G VALUES OF 3-AMINO-1,2-CYCLOHEXANEDIOL DERIVATIVES

Compound		M_G
3α-Amino-1α,2β-cyclohexanediol	N-*p*-Nitrobenzoyl derivative	0.00
	N-Phenylthiourea derivative	0.00
3β-Amino-1α,2α-cyclohexanediol	N-*p*-Nitrobenzoyl derivative	0.34
	N-Phenylthiourea derivative	0.44

taining 0.1 *M* sodium tetraborate solution, and a voltage of 435 at 75 ma was applied for 1 hour. The strips were dried at 100° on a glass plate and sprayed with alkaline permanganate (34) giving yellow spots on a pink to greenish-pink background. The M_G values of the compounds studied are shown in Table VII.

ACKNOWLEDGMENTS

We are indebted to Mr. A. A. Casselman for performing the paper chromatograms described herein, to Mr. R. O. Braun for preparation of a quantity of 1-ethoxycyclohexene-2 chlorohydrin, to Dr. C. E. Hubley and Mr. A. Grey for measurement of the infrared spectra, to Dr. C. T. Bishop for assistance with the electrophoretic experiments, and to Dr. R. U. Lemieux and Dr. R. Y. Moir for a number of helpful discussions.

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THE REACTION OF CYANOGEN BROMIDE WITH THE SODIUM SALTS OF CARBOXYLIC ACIDS

II. THE REACTION OF CYANOGEN BROMIDE WITH THE SODIUM SALTS OF ALIPHATIC ACIDS[1]

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ABSTRACT

Cyanogen bromide reacts with the sodium salts of lower aliphatic acids at 250–300° C to form an α-keto isocyanate as the primary product. The latter undergoes subsequent pyrolytic decomposition to a nitrile and carbon dioxide. A mechanism is proposed to account for the observed interchange of labelled carbon atoms between the CN group of the cyanogen bromide and the carboxyl group of the salt in the over-all reaction.

INTRODUCTION

In the heterogeneous reaction between cyanogen bromide and sodium benzoate at 250–300° C, it was shown, by the use of carbon-14-labelled reactants, that an interchange of carbon atoms between the CN group of the cyanogen bromide and the carboxyl group of the benzoate occurs according to the following over-all reaction (1):

$$CNBr + RC^*OONa \rightarrow RC^*N + CO_2 + NaBr. \qquad [1]$$

Preliminary experiments with sodium salts of several aliphatic acids and cyanogen bromide under similar conditions (2) seemed to indicate that a different mechanism was in operation, since a significant portion of carbon dioxide carbon originated in the aliphatic carboxyl group. In a more detailed investigation, however, which is described in this communication, it was established that the interchange of carbon atoms in accordance with reaction [1] occurs also when R is aliphatic (R = CH_3, C_2H_5—), although other simultaneously occurring pyrolytic reactions tend to obscure this reaction.

Although the sodium salts of several aliphatic acids were employed in this study, the most significant observations were made with sodium propionate as a reactant. Upon reaction with cyanogen bromide at 250–300° C under the conditions described previously, the latter salt yielded, in addition to the expected propionitrile, carbon dioxide and sodium bromide, two other compounds. Dipropionamide collected as a sublimate in the cooler part of the apparatus.[4] The other product was collected along with propionitrile in the cold trap attached to the pyrolysis tube. Unlike a nitrile, this compound reacted readily with ammonia under anhydrous conditions. The latter material possessed the properties of propionylurea, forming carbon dioxide and acid upon alkaline hydrolysis. In an experiment in which sodium acetate was the starting material, the nitrile fraction was passed through a mixture of glass and fuller's earth at 300° C. The formation of some carbon dioxide afforded additional evidence that the primary product of the reaction of cyanogen bromide with the sodium salt of an aliphatic acid is a compound yielding nitrile and carbon dioxide on pyrolysis, and forming monoacylurea with anhydrous ammonia. This primary product is an α-keto isocyanate, on the basis of the foregoing evidence.

[1]*Manuscript received May 8, 1958.*
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[3]*Present Address: Faculty of Medicine, Queen's University, Kingston, Ontario.*
[4]*Zappi and Bouso (3) have reported the formation of monoamides in the reaction of sodium acetate and sodium propionate with cyanogen chloride.*

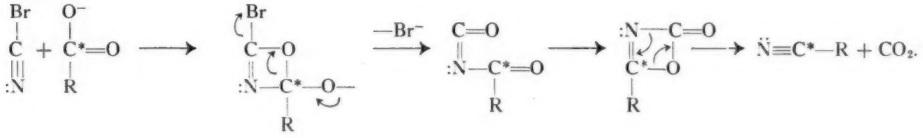
The reaction of cyanogen bromide with the sodium salt of an aliphatic acid may therefore be summarized as follows:

$$CNBr + RCOONa \rightarrow RCONCO + NaBr$$

$$RCONCO \rightarrow RCN + CO_2.$$

Only with lower aliphatic acids and under high vacuum is it possible for some of the α-keto isocyanate to escape complete pyrolysis. In the previously investigated reaction of sodium benzoate with cyanogen bromide, benzoyl isocyanate is undoubtedly formed initially, but it immediately pyrolyzes because of its low volatility.

To explain the observed interchange of carbon atoms between the CN group of the cyanogen bromide and the carboxyl group, the following mechanism is postulated:



An investigation of the pyrolysis of pure propionyl (isocyanate-C^{14}) should confirm this mechanism.

EXPERIMENTAL

The apparatus and procedure have already been described in detail (1). Approximately one millimole of the aliphatic acid sodium salt was weighed out and was suspended on a mixture of 0.5 g each of ignited fuller's earth and pulverized glass (40 mesh) by evaporation of a slurry of these materials in water. When a C^{14}-labelled sodium salt was employed, a known amount of activity was added to the weighed sample of inactive sodium salt in solution, before the latter was mixed with the fuller's earth and glass. After evaporation of the slurry, the mixture was transferred to the U-tube of the pyrolysis apparatus, and was heated in a Wood's metal bath to the appropriate temperature. The pyrolysis tube was connected, through a spiral trap cooled in liquid nitrogen, to a high-vacuum line. Slightly more than the equivalent quantity of cyanogen bromide was allowed to diffuse through the contents of the U-tube, while the latter was evacuated continuously. The carbon dioxide which collected in the spiral was converted to barium carbonate after fractionation with dry ice – acetone. The nitrile fraction was partially separated from unreacted cyanogen bromide by distillation on the vacuum line, and was reduced in ethereal solution with lithium aluminum hydride for characterization and radioassay. After decomposition of the lithium aluminum complex with dilute sulphuric acid, the amine was distilled from the mixture, after the latter had been rendered alkaline with sodium hydroxide, in a semimicro-Kjeldahl apparatus. The distillate was collected in excess dilute hydrochloric acid. The amine hydrochloride remaining after evaporation of this solution was recrystallized from an appropriate solvent. Ethanol was employed for ethylamine hydrochloride, and chloroform for propylamine and higher amine hydrochlorides. Known amounts of the hydrochlorides were plated on stainless-steel planchets for radioassay. Stearonitrile was plated directly, after purification by high-vacuum sublimation. Barium carbonate was plated on aluminum disks from a slurry. Appropriate self-absorption corrections were applied where necessary (4). Counting was performed with a helium and alcohol flow-type geiger counter with an approximately 2π geometry.

Pyrolysis of Nitrile Fraction from an Experiment with Sodium Acetate

Sodium acetate (4 millimoles) was suspended on powdered glass (40 mesh), and this mixture was placed in the U-tube of the apparatus previously described. Cyanogen bromide in slight excess was passed through the U-tube while the latter was evacuated continuously. Carbon dioxide was fractionated with dry ice – acetone and converted to barium carbonate. Yield of $BaCO_3$ 0.2227 g (28% based on acetate). The liquid remaining in the spiral trap was recycled through a mixture of fuller's earth and powdered glass at 304° C under high vacuum. An additional quantity of carbon dioxide was formed during pyrolysis, yielding 0.0945 g of barium carbonate.

Alkaline Hydrolysis of Propionylurea

The liquid reaction product from two experiments in which sodium propionate-1-C^{14} was allowed to react with cyanogen bromide under the conditions previously described was treated with ammonia in ether under anhydrous conditions. To the solid obtained from this reaction was added carrier propionylurea (5), the mixture was homogenized by crystallization, and the solid was sublimed under high vacuum. To a solution of the sublimate (5.15 mg) was added carrier propionylurea (25.9 mg) and the whole was evaporated to dryness in a bomb tube. The residue was hydrolyzed with saturated barium hydroxide solution (4 ml) at 100° C in the sealed tube overnight. A quantitative yield (52.7 mg) of barium carbonate was obtained, of specific activity 22,850 counts/minute millimole. The specific activity of the material before hydrolysis was 32,800 counts/minute millimole. A small portion of the initial activity was present in the acid recovered from the hydrolysis.

PAPER CHROMATOGRAPHY OF AMINE HYDROCHLORIDES AND OTHER COMPOUNDS

The amine hydrochlorides obtained from the lithium aluminum hydride reduction of the product nitriles were chromatographed on Whatman No. 1 filter paper by the ascending technique. For comparison, authentic samples of amine hydrochlorides were run in adjacent positions. Butanol saturated with 25% aqueous acetic acid was the developing solvent. The amines were detected with ninhydrin (6).

Propionylurea could not be distinguished from propionamide when these substances were chromatographed with the butanol – acetic acid – water medium as both had R_f values of 0.74. To facilitate detection on paper, these compounds were labelled with carbon-14 by synthesis from propionic acid-1-C^{14}. The developed chromatograms were placed in contact with Eastman No-Screen X-Ray film.

Dipropionamide-1-C^{14} with butanol–water as the developing solvent had an R_f of 0.91. Several unidentified spots with R_f values less than 0.74 appeared faintly on radioautographs of chromatograms of the nitrile fraction from the sodium propionate – cyanogen bromide reaction after this fraction had been treated with anhydrous ammonia. α-Cyanopropionic acid and α-isocyanopropionic acid were shown to be absent by chromatography of these substances for comparison.

RESULTS AND DISCUSSION

Data for typical experiments are presented in Tables I and II. It is evident that a significant portion of the carbon dioxide carbon is derived from the cyanogen bromide molecule. Simultaneously occurring pyrolytic reactions, other than the formation of an α-keto isocyanate and its decomposition to a nitrile and carbon dioxide, may explain in part the distribution of radioactivity among the products. Moreover, the formation and

pyrolysis of a part of the α-keto isocyanate by a route other than the postulated one, could also account for this distribution of activity. Such reactions as decarboxylation

TABLE I

DATA FOR THE REACTION OF CNBr WITH SODIUM SALTS OF C^{14}-CARBOXYL ACIDS

Salt	Temperature, °C	Specific activities counts/minute millimole			Amine from reduction of nitrile
		Na salt	$BaCO_3$	Amine salt	
Sodium acetate	274–277	21,000	4,740	15,200	Ethylamine
		17,650	8,120	—	
		17,650	1,675	—	
Sodium propionate	267–273	48,100	6,440	47,700	Propylamine
Sodium butyrate	300–303	453,300	44,400	321,500	Butylamine
Sodium valerate	300–303	64,400	10,230	64,000	*n*-Amylamine
Sodium stearate	274–277	79,500	38,300	53,000*	

*Stearonitrile was counted directly, after purification by distillation from a Späth bulb *in vacuo*.

TABLE II

DATA FOR THE REACTION OF C^{14}-NBr WITH SODIUM SALTS OF CARBOXYLIC ACIDS

Salt	Temperature, °C	Specific activities counts/minute millimole		
		CNBr	$BaCO_3$	Amine salt
Sodium acetate	270–271	163,000	72,300	73,300
Sodium propionate	271–272	163,000	69,900	13,800
Sodium butyrate	267–274	163,000	53,100	6,060
Sodium trimethylacetate	294–297	883,000	576,000	231 counts/minute mg (Unidentified reduced product)
Sodium α-bromopropionate	287–291	318,200	29,080	—

and dehydration as well as the formation of free aliphatic acid in the presence of traces of hydrogen bromide are all possible under the experimental conditions employed, and one or more of these is probably responsible for the observed formation of a diamide. Variation in reaction conditions from one aliphatic acid to another is in part the result of the decreasing volatility of the intermediate α-keto isocyanate with increasing molecular weight. Thus, this intermediate was present in the nitrile fractions from the sodium acetate and propionate reactions, but with higher acids, and especially with benzoic acid, the α-keto isocyanate could have only a momentary existence in the hot zone of the pyrolysis apparatus. The postulated formation of an α-keto isocyanate in the reactions investigated offers a logical explanation of the observed interchange of carbon atoms between cyanogen bromide and the carboxyl group through the mechanism described earlier in this communication.

ACKNOWLEDGMENT

The authors wish to thank Dr. Karl Wiesner for his helpful criticism and advice.

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STUDIES ON THE MECHANISMS OF CYCLIZATION OF RING A OF STEROIDS DURING THE REFORMATSKY REACTION[1]

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ABSTRACT

The Reformatsky reaction of 3,5-*seco*-5-ketocholestan-3-oic acid methyl ester with methyl bromoacetate yielded 2-carbohydroxycholestenone, cholestenone, and 4-carbomethoxycholestenone. The appearance of these products indicated that cyclization of ring A proceeded along two different paths; this conclusion was confirmed by the use of methyl bromoacetate-1-C^{14} and -2-C^{14}.

One of the earliest successful attempts (1) at introduction of radioactive carbon 14 into ring A of the steroid nucleus involved the Reformatsky reaction of 3,5-*seco*-5-ketocholestan-3-oic acid methyl ester (I*b*) with carboxyl-labelled methyl bromoacetate. In these experiments, the crude Reformatsky products were cyclized, hydrolyzed, and decarboxylated by conventional methods to provide cholestenone-3-C^{14} (XI*) in 32% yield. The molar radioactivity count of XI* was found to be the same as that of the carboxyl-labelled methyl bromoacetate used, and largely on the basis of this finding the conclusion was reached that the reaction proceeded entirely through the intermediates III*, IV*, and V*. This sequence of reactions was postulated by Turner (1) to involve abstraction of a proton from III* at position 2, followed by transannular ring closure and elimination of methoxide ion to give the keto-lactone IV*. The latter, in turn, would then lose a proton at position 4 and be transformed readily into the stable anion V*. It was also pointed out that removal of a proton, alpha to the carbomethoxy group in III*, would lead to a less stable four-membered oxygen intermediate; the latter, after hydrolysis and dehydration, would be expected to decarboxylate yielding inactive cholestenone (XI). There is considerable evidence in support of Turner's view that Reformatsky reactions of δ-ketoesters can provide intermediate lactones of the type III. Thus, it was shown (2) that methyl β-(1-methyl-2-ketocyclohexyl)propionate and ethyl bromoacetate reacted under the usual Reformatsky conditions to yield 21% of 2-keto-3-carboxy-10-methyl-$\Delta^{1,9}$-octahydronaphthalene. The isolation of this acid by extraction from the crude reaction products with 2% ammonium hydroxide can only be explained by assuming the formation of an intermediate six-membered lactone. Similarly, 1-tetralone-2-β-propionic acid methyl ester on treatment with methyl bromoacetate and zinc provided 1-acetic acid methyl ester-3,4-dihydronaphthalene-2-β-propionic acid (3). It has been known for long that γ-ketoesters undergo Reformatsky reactions to yield γ-lactones. Ethyl levulinate, for example, was found to afford amongst other products the lactone of β-hydroxy-α,β-dimethyladipate, when condensed with methyl α-bromopropionate (4). Ethyl β,β-dimethyllevulinate and ethyl bromoacetate produced over 50% of δ-carbethoxy-β,β,γ-trimethyl-γ-valerolactone (5).

The studies to be described herewith were undertaken to determine more conclusively the mechanisms of ring closure during the Reformatsky reaction of the δ-ketoester I*b*.

[1]*Manuscript received April 25, 1958.*
Contribution from the Department of Biochemistry, McGill University, Montreal, Quebec. Much of this work was done by P. Ziegler as part of the requirements for the Ph.D. degree.
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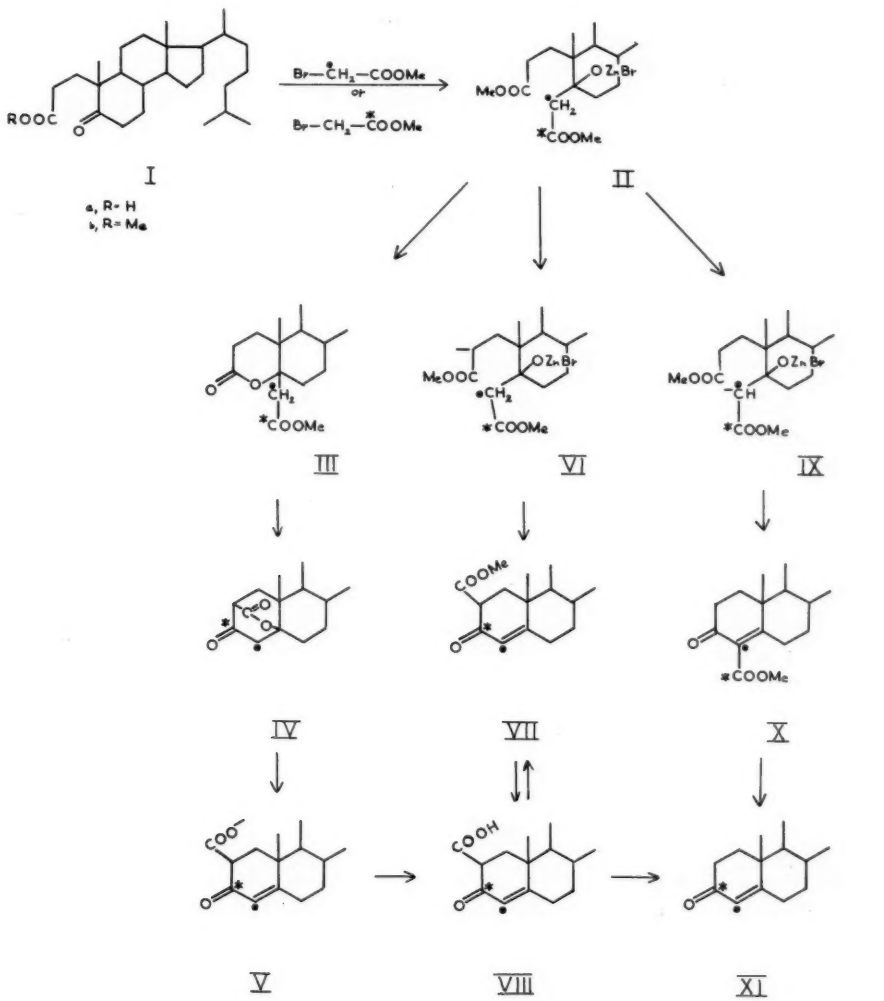

The experiments were usually carried out in refluxing benzene using tracer amounts of C^{14}-labelled methyl bromoacetate, and the products, from which zinc salts were removed by washings with dilute mineral acid, were finally chromatographed on neutral alumina. Elution from the column with hexane–benzene separated four different compounds. The first fraction consisted of cholestenone (XI* or XI•), identified by melting point, optical rotation, ultraviolet absorption, and comparison with an authentic specimen of XI. Regardless of whether methyl bromoacetate-1-C^{14} or -2-C^{14} was employed, the crystals of cholestenone proved to be radioactive. The second compound obtained from the alumina failed to crystallize and was not radioactive; it was saponified to give I*a*, and therefore represented unreacted starting material. The third fraction was a crystalline solid which was radioactive, both when methyl bromoacetate-1-C^{14} and -2-C^{14} were

used. It analyzed correctly for a carbomethoxycholestenone, and on the basis of the following evidence could be quite definitively assigned the structure of 4-carbomethoxycholestenone (X* or X•). The material exhibited maximum absorption in the ultraviolet region at 243.5 mμ (log ϵ = 4.14), characteristic of an α,β-unsaturated ketone. The known fact (2) that the presence of a carbomethoxy group in cross-conjugation with an α,β-unsaturated ketone does not affect the latter's absorption maximum in the ultraviolet should be noted in this case. Examination in the infrared region showed bands at 5.74 μ and at 5.95 μ, representative of the carbonyl group of an ester and a Δ^4-3-ketone respectively. The compound did not give a coloration with alcoholic ferric chloride solution and failed to react with sodium in benzene; this evidence, indicative of the absence of an active hydrogen, can be accommodated by 4-carbomethoxycholestenone (X), but not by its isomer VII. While the unknown compound, assigned structure X, was resistant to alkaline hydrolysis, probably because its resonance structures do not permit nucleophilic attack at the exocyclic carbon atom attached to C-4, it readily provided cholestenone on acid treatment. The isomer VII on the other hand would be expected to saponify in the normal fashion, since resonance in this system does not prevent carbonium ion formation at the exocyclic carbon atom attached to C-2; in fact, it was found that 2-carbomethoxycholestenone (VII) saponified readily under mild conditions. That the unknown compound was indeed 4-carbomethoxycholestenone (X) was shown conclusively by the tracer technique. It was found that acid hydrolysis of the carbomethoxycholestenone, obtained with methyl bromoacetate-2-C^{14}, gave rise to radioactive cholestenone (XI•); however, the acid hydrolysis of the intermediate obtained with methyl bromoacetate-1-C^{14} provided inactive cholestenone (XI).

The fourth and last compound eluted from the column of alumina was found to contain twice the radioactivity count of XI• (or XI*) and X• (or X*) obtained in the same experiment. It was therefore assumed that 2 moles of acetate had been incorporated into its structure. Since cholestenone could not be derived from it by acid or alkaline treatment, this compound was not examined further.

In one Reformatsky reaction, using inactive reagent, the crude products were analyzed for the presence of Δ^4-3-ketone by ultraviolet spectrophotometry, both before and after treatment with cold dilute acid. Since the two assays showed the presence of 30–35% of Δ^4-3-ketone, it was concluded that cyclization and elimination of bromozinc methoxide occurred during the Reformatsky reaction, and not on acidification or chromatography on alumina. That Dieckmann type cyclizations occur during Reformatsky reactions with δ-keto esters has previously been reported (6, 7, 8). It was of interest to note that these analytical figures agreed well with the amounts of Δ^4-3-ketones (XI plus X) usually isolated from the chromatograms. The reaction products were then separated into neutral and acidic constituents by washing with dilute sodium carbonate solution; the two fractions contained 23% and 8% of Δ^4-3-ketones respectively. The acid fraction was crystallized to yield a compound, m.p. 126–128° C, giving an intense green color with ferric chloride solution. It was assigned structure VIII on the basis of this evidence and because it provided cholestenone (XI) on pyrolysis. Methylation of VIII afforded the corresponding methyl ester (VII), which also produced a green coloration with ferric chloride solution and showed an ultraviolet absorption maximum at 244.5 mμ (log ϵ = 4.21). Elemental analyses for VII (and its 2,4-dinitrophenylhydrazone) were not entirely satisfactory, probably because of contamination with traces of cholestenone. On mild saponification, VII yielded VIII.

A careful examination of these results proves that, under the experimental conditions used, two different mechanisms of cyclization are operative. When the Reformatsky

reaction was carried out with methyl bromoacetate-1-C^{14}, the cholestenone (XI*) and the 4-carbomethoxycholestenone (X*), isolated from the column of alumina, were both radioactive. Since acid hydrolysis of X* yielded inactive XI, the reaction path leading to X* must be different from that leading to XI*. In other words, 4-carbomethoxycholestenone (X) is not the precursor of the cholestenone eluted from the chromatograms. The sequence of reactions leading to the formation of X is postulated to proceed by a Dieckmann cyclization of the Reformatsky ester II, via the intermediate IX. The isolation of 2-carbohydroxycholestenone (VIII) from the alkaline washings of the reaction products and the demonstration of its facile decarboxylation indicate that VIII is the precursor of the cholestenone eluted from the chromatogram. The isolation of the acid VIII lends support to Turner's hypothesis (1) of the formation of the intermediate lactonic ester III. Dieckmann cyclization of the Reformatsky ester II via VI (in the opposite sense as was postulated before) would be expected to provide VII. But since VII failed to appear amongst the isolated reaction products, the second mechanism of cyclization is believed to proceed via the intermediates III, IV, V, and VIII. In conclusion, it should be noted that the two different cyclization reactions occur to the same extent, as judged by the yields of X and XI.

EXPERIMENTAL

All melting points have been corrected. The optical rotations were determined in chloroform solution, the ultraviolet spectra in ethanol (unless otherwise stated), and the infrared spectra, obtained by Dr. R. N. Jones, of the National Research Council, Ottawa, in carbon disulphide. Microanalyses were carried out by Mr. E. Thommen, Basel, Switzerland.

Methyl bromoacetate-1-C^{14} and -2-C^{14} were kindly prepared by Dr. B. Belleau; the radioactivity counts of these reagents are not known. The radioactivities of the steroids were determined in the flow Q-gas counter (Nuclear Instrument and Chemical Corporation) and are expressed in counts per minute per milligram.

Cholestenone-4-C^{14} (XI) and 4-Carbomethoxycholestenone-4-C^{14} (X*)*

3,5-*seco*-5-Ketocholestan-3-oic acid (I*a*; 5 g; 12.3 millimoles) was treated with an ethereal solution of diazomethane, the ether was evaporated, and the residual oil dried *in vacuo*. Absolute anhydrous benzene (50 ml), a crystal of iodine, activated zinc (2.5 g), and methyl bromoacetate-2-C^{14} (3.8 g; 25 millimoles) were added to the dried residue. The mixture was refluxed for 3.5 hours, during which time a white, crystalline precipitate formed and gradually the solution turned brown. More activated zinc (1.5 g) was added during the first ½ hour of refluxing. After it had been cooled, the mixture was diluted with ether and dilute hydrochloric acid, the solvent extract was washed five times with dilute acid, then with water, dried over sodium sulphate, filtered, and evaporated to dryness. The yellow, oily residue (4.65 g) could not be crystallized; it was methylated with diazomethane and subsequently chromatographed on activated alumina (100 g), using 200 ml portions of eluant.

Fractions 5–11 were combined to yield, after recrystallization from ether–methanol, 650 mg (14%) of cholestenone-4-C^{14} (XI*), m.p. 79–80°, $[\alpha]_D^{19}$ +89.9°, showing maximum ultraviolet absorption at 242.5 mμ (log ϵ = 4.18) and counting at 3200.

Fractions 12–19 could not be crystallized; they were saponified for 2 hours with 5% methanolic potassium hydroxide to yield, after working up, 930 mg (19%) of crystals, m.p. 155°, giving no depression on mixed melting point with authentic 3,5-*seco*-5-ketocholestan-3-oic acid (I*a*). This recovered starting material was not radioactive.

Fraction No.	Eluant in % by volume		Eluate		
	Hexane	Benzene	Weight, mg	M.p.	Counts $min^{-1} mg^{-1}$
1–4	100	0	3	oil	—
5–11	87.5	12.5	887	79–80	3200
12–19	70	30	1300	oil	0
20–26	50	50	746	154	3600
27–32	40	60	432	154	
33–38	25	75	420	155	6800
39–43	10	90	252	155	
44–47	0	100	166	153	
48–49	100 Ether		150	oil	—
50–51	100 Methanol		224	oil	—
			4580		

Fractions 20–32 were crystallized from ether–hexane to provide 850 mg (16%) of 4-carbomethoxycholestenone-4-C^{14} (X*), m.p. 154° and $[\alpha]_D^{19}$ +89.4°; this compound gave no coloration with tetranitromethane or alcoholic ferric chloride, did not react with sodium in benzene, but developed a purple color with the Zimmermann reagent; it showed an ultraviolet maximum at 243.5 mμ (log ϵ = 4.14) and in the infrared region its maxima were at 5.75 μ and 5.95 μ. Anal. Calc. for $C_{29}H_{46}O_3$: C, 78.68; H, 10.47; OCH_3, 7.01. Found: C, 78.89; H, 10.48; OCH_3, 6.90.

Fractions 33–47, crystallized from ether–hexane, yielded 650 mg (10%) of material, m.p. 155°, and gave marked depression on mixed melting point with *Ia* and X*. This material gave no color reactions with alcoholic ferric chloride, tetranitromethane, or the Zimmermann reagent and was transparent through the ultraviolet range of the spectrum. Its radioactivity count was 6800. Attempts at conversion of this compound to cholestenone by vacuum distillation, saponification, or acid hydrolysis failed. Microanalyses indicated the presence of one methoxy group and the formula $C_{31}H_{50}O_5$.

2,4-Dinitro-phenylhydrazone of X

Compound X (100 mg) and 2,4-dinitro-phenylhydrazine (300 mg) were refluxed for 15 minutes in 95% ethanol (30 ml). The hot solution was then treated with concentrated hydrochloric acid (2 ml) and refluxed for an additional 15 minutes. After it had been cooled, the precipitate was filtered off, washed with ethanol, then with hexane, and dried. The orange hydrazone had m.p. 198–200°. Anal. Calc. for $C_{35}H_{50}O_6N_4$: C, 67.50; H, 8.09; N, 9.00. Found: C, 67.49; H, 8.35; N, 9.25.

Acid Hydrolysis of 4-Carbomethoxycholestenone-4-C^{14} (X)*

Compound X* (200 mg) was refluxed for 15 hours in glacial acetic acid (12.5 ml) and concentrated hydrochloric acid (3 ml). The solution was then diluted with water, extracted with ether, and the solvent extract washed twice with water, three times with dilute sodium carbonate, and again with water. The ether solution was dried, then evaporated to yield 170 mg of an oily residue which on crystallization from ether–methanol gave 147 mg (85%) of cholestenone-4-C^{14} (XI*), m.p. 79–80°, and counting at 4000.

Saponification of 4-Carbomethoxycholestenone (X)

The ester X (200 mg) was refluxed for 2 hours in 5% methanolic potassium hydroxide (20 ml). After addition of water, most of the methanol was evaporated *in vacuo* and the residue was extracted with ether. The solvent extract, washed with water to neutrality,

yielded, after drying over sodium sulphate, filtration, and evaporation of the ether, 172 mg of material; this was crystallized from methanol to give unreacted starting material, m.p. 153–154°, no depression on mixed melting point with X.

Cholestenone-3-C^{14} (XI) and 4-Carbomethoxycholestenone-C^{14} (X*)*

The experimental procedure employed was the same as that described for the preparation of X' and XI', except that different quantities of reagents were used and that carboxyl-labelled methyl bromoacetate was substituted for the corresponding methylene-labelled compound.

The dry residue obtained after methylation of I*a* (3 g; 7.4 millimoles) was reacted with zinc (2 g), a crystal of iodine, and methyl bromoacetate-1-C^{14} (2.28 g; 14.9 millimoles) in benzene (35 ml). Chromatography of the products yielded 245 mg (9%) of cholestenone-3-C^{14} (XI*), m.p. 79–81°, counting at 1.5×10^4 min^{-1} mg^{-1}; 1.02 g (34%) of non-radioactive starting material (I*a*), m.p. 153–154°; 205 mg (8%) of 4-carbomethoxycholestenone-C^{14} (X*), m.p. 154° and counting at 1.4×10^4 min^{-1} mg^{-1}; 160 mg (4%) of material, m.p. 154–155°, counting at 2.4×10^4 min^{-1} mg^{-1}.

Acid Hydrolysis of 4-Carbomethoxycholestenone-C^{14} (X)*

Compound X* (100 mg), m.p. 154° and counting at 1.4×10^4 min^{-1} mg^{-1}, was refluxed for 15 hours with glacial acetic acid (7.5 ml), concentrated hydrochloric acid (4 ml), and dioxane (2 ml). The solution was diluted with water and extracted with ether, the solvent extract was washed successively with water, dilute carbonate, and again with water. The neutral ethereal solution was dried over sodium sulphate, filtered, and evaporated to yield 98 mg of an oily residue, which was chromatographed on 5 g of alumina, using 10-ml portions of eluant. The fractions, obtained with benzene–hexane (3:7, 1:1, and 4:1), were crystallized from ether–methanol to provide 70 mg of cholestenone (XI), m.p. 80° and counting at 80 min^{-1} mg^{-1}. This very low activity could not be removed either by vacuum distillation of a sample of this cholestenone or by repeated crystallization from ether–methanol; it is attributed to slight contamination. Further elution of the alumina column with benzene and ether yielded 27 mg of residue. This material was crystallized from ether–hexane to give unreacted starting material, m.p. 149–152°, with a radioactivity of 1.5×10^4; it did not give a depression on mixed melting point with X*.

Quantitative Analysis for α,β-Unsaturated 3-Ketones in the Products of the Reformatsky Reaction by Ultraviolet Spectrophotometry

3,5-*seco*-5-Ketocholestan-3-oic acid (I*a*; 3 g; 7.4 millimoles) was methylated with ethereal diazomethane and the ether evaporated. The residue, after thorough drying *in vacuo*, was then dissolved in anhydrous benzene (30 ml) and treated with zinc (2 g), a crystal of iodine, and methyl bromoacetate (2.28 g; 14.9 millimoles). This mixture was refluxed gently for 2 hours, then cooled. A sample (0.1 ml), pipetted out of the solution, was evaporated to remove the benzene, and then dissolved in anhydrous ether (100 ml). This ethereal solution showed an ultraviolet maximum at 243 mμ ($\log I_0/I_x = 1.44$). On the basis of molecular weight (400) and extinction coefficient (15,000), 0.96 g of Δ^4-3-ketone was calculated to be present.

The benzene solution was then diluted with ether and cold dilute hydrochloric acid, the aqueous layer was discarded, and the solvent extract washed with water. Again a sample (0.25 ml) was pipetted out of the ether–benzene extract (72 ml), the solvents were evaporated, and the residue from the sample dissolved in ethanol (100 ml). This

solution exhibited an ultraviolet maximum at 242 mμ (log $I_0/I_x = 1.2$); it was therefore calculated that 0.92 g of Δ^4-3-ketone was contained in the crude acidified Reformatsky reaction products.

The ether–benzene extract, after dilution with more ether, was washed three times with portions (30 ml) of 5% sodium carbonate solution, then with water until the washings were neutral. A sample (0.54 ml) of the neutral solvent phase (135 ml) was evaporated *in vacuo* and the residue dissolved in ethanol (100 ml). The alcoholic solution showed a maximum in the ultraviolet at 242 mμ (log $I_0/I_x = 1.05$), indicating that 0.7 g of Δ^4-3-ketone was present in the neutral solvent extract.

The carbonate washings were acidified immediately, extracted with ether, and the solvent extract washed several times with water; it was dried over sodium sulphate, filtered, and finally evaporated to dryness to yield an oily residue (275 mg). A small part (3 mg) of this residue was dissolved in 100 ml of ethanol; the resulting solution showed an ultraviolet maximum at 242 mμ (log $I_0/I_x = 0.93$), which demonstrated the presence of 230 mg of Δ^4-3-ketone in the acid fraction.

Isolation of 2-Carbohydroxycholestenone (VIII)

The acid fraction (275 mg), obtained in the preceding experiment, was crystallized from ether–hexane to yield 100 mg of material, m.p. 118–121°; recrystallization from ether gave m.p. 126–128° (the melted crystals resolidified on cooling, then remelted at 75–85°). This substance gave a yellow color with tetranitromethane, an intense green with alcoholic ferric chloride, but was negative in the Zimmermann test. It exhibited a maximum absorption in the ultraviolet at 242 mμ (log $\epsilon = 4.23$).

The mother liquor of this acid fraction on standing in aqueous ethanol gave cholestenone (XI), m.p. 81–82°, no depression on mixed melting point with authentic XI. It was therefore concluded that VIII decarboxylated partially during extraction and/or isolation procedures.

Pyrolysis of VIII

Distillation of VIII, m.p. 126–128°, *in vacuo* (0.1 mm) at 185–193° provided a distillate which readily crystallized from ether–methanol to yield quantitatively cholestenone (XI), m.p. 78–80°.

2-Carbomethoxycholestenone (VII)

Compound VIII was methylated with ethereal diazomethane, the ether solution washed with water, dried over sodium sulphate, filtered, and the filtrate evaporated *in vacuo*. The residue crystallized with difficulty from aqueous methanol to give a substance (VII) of m.p. 91–93°; recrystallization from methanol gave m.p. 102–104° and $[\alpha]_D^{19}$ +91°. This material produced a green color with ferric chloride solution, showed an ultraviolet maximum at 244.5 mμ (log $\epsilon = 4.21$), and exhibited carbonyl absorption bands in the infrared region at 5.73 μ and at 5.96 μ. Anal. Calc. for $C_{29}H_{46}O_3$: C, 78.68; H, 10.47. Found: C, 79.07; H, 10.95.

2,4-Dinitro-phenylhydrazone of VII

A solution of VII (40 mg) and 2,4-dinitro-phenylhydrazine (150 mg) in ethanol (35 ml) was refluxed for ½ hour. After cooling, concentrated hydrochloric acid (2 ml) was added and the solution was then kept at 20° for several hours. The precipitate which had formed was filtered off, washed with ethanol and hexane, and dried *in vacuo*. The orange crystals had m.p. 213–215°. Anal. Calc. for $C_{35}H_{50}O_6N_4$: C, 67.50; H, 8.09; N, 9.00. Found: C, 66.68; H, 7.91; N, 8.92.

Saponification of 2-Carbomethoxycholestenone (VII)

Compound VII (75 mg) and potassium carbonate (50 mg) were dissolved in methanol (15 ml) and water (1 ml). The solution, after standing at 20° for 48 hours, was diluted with water and extracted with ether. The solvent extract provided a neutral fraction (22 mg) which failed to crystallize; the acid fraction (50 mg), obtained from the aqueous carbonate phase, crystallized from ether, giving material of m.p. 124–125°. This substance (VIII) gave no depression on mixed melting point with VIII.

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THE SOLUBILITY OF ALUMINUM HYDROXIDE IN ACIDIC AND BASIC MEDIA AT 25° C[1, 2]

K. H. Gayer, L. C. Thompson, and O. T. Zajicek

ABSTRACT

The solubility of $Al(OH)_3$ was measured in NaOH and $HClO_4$ solutions. Possible reactions of $Al(OH)_3$ in dilute NaOH and $HClO_4$ solutions are indicated along with the calculated constants. The amphoteric hydroxide was found to be more acidic than basic. The isoelectric point of $Al(OH)_3$ was determined to be pH 7.7.

HISTORICAL

The amphoteric nature of aluminum hydroxide has been studied by other investigators, but owing to incomplete data the extent of its amphoterism is still not entirely determined. Its isoelectric point has not been previously determined.

A number of equilibrium constant values are tabulated below:

Source	Equilibrium constant	Value
Heyrovsky (1)	Solubility product	1.06×10^{-33} at 25° C
Heyrovsky (1)	Ion product of aluminic acid	35×10^{-14} at 25° C
Kruyt and Troelstra (2)	Solubility product	1.00×10^{-32} at 25° C
Wood (3)	Acid dissociation constant	6.30×10^{-13} at 25° C
Slade (4)	Acid monobasic dissociation product approx. constant	1×10^{-10}

Hildebrand (5), in his study on the solubility of aluminum hydroxide, claimed that it dissolved as an acid. This claim was supported by the slight break in the solubility curve corresponding to the addition of another equivalent of base. Heyrovsky (6) stated that aluminum hydroxide dissolves in alkalies as follows:

$$Al(OH)_3 + OH^- \leftrightarrows Al(OH)_4^-.$$

Joseph (7) in plotting equivalent conductance against the ratio of sodium hydroxide to aluminum hydroxide obtained no sharp breaks or irregularities and, therefore, concluded that aluminate ion AlO_2^- occurs.

EXPERIMENTAL

Procedure

The general procedure is similar to that used by Garrett and Heiks (8).

Preparation of Reagents

The preparation of conductivity water is that of Gayer and Woontner (9).

Aluminum hydroxide.—Aluminum hydroxide was precipitated from aluminum chloride by means of sodium hydroxide. The precipitate was washed several times beyond that required to give a negative flame test for sodium for both the solid and the supernatant liquid. A sample of the precipitate was dried for 2 days at 50° C. Following this, it was ignited at 500° C. From the weight loss, the empirical formula was calculated to be

[1]*Manuscript received April 8, 1958.*
Contribution from the Chemistry Department, Wayne State University, Detroit, Michigan.

[2]*From a dissertation submitted by Mr. Lancelot C. Thompson in partial fulfillment of the requirements for the Doctor of Philosophy degree and a dissertation submitted by Mr. O. T. Zajicek in partial fulfillment of the requirement for the Master of Science degree.*

$Al_2O_3 \cdot 3H_2O$. An X-ray diffraction powder pattern showed the material to be crystalline. The three major d values, in order of decreasing intensity, were found to be 4.62, 4.27, and 2.20 Å.

Aluminum chloride.—Baker and Adamson reagent grade aluminum chloride crystals were used to prepare the hydroxide. Standard aluminum solutions: 1.76 g of aluminum alum was dissolved in distilled water and made up to 1 liter. The standard solution contained 0.1 mg of aluminum per milliliter. From this solution spectrophotometric determinations of aluminum were made by diluting to make solutions of 2, 4, 8, 12, 16, 20, 24, and 28 γ/ml. The standard curve was prepared by means of the Beckman Model B spectrophotometer.

Chloroform.—Reagent grade chloroform was used for the extraction of the aluminum quinolate.

8-Hydroxyquinoline.—Twenty grams of hydroxyquinoline was dissolved in 60 ml of glacial acetic acid and diluted to 1 liter with distilled water.

Colorimetric analyses.—The aluminum analyses were made with a Beckman Model B spectrophotometer using the method of Sherrington and Gentry (10). The absorbance was measured at 400 mμ against a reagent blank.

pH.—A Beckman Model G pH meter was used to determine the equilibrium values of the hydrogen and hydroxyl ion activities.

TABLE I

SOLUBILITY OF ALUMINUM HYDROXIDE IN SODIUM HYDROXIDE SOLUTIONS AT 25° C

Initial moles NaOH/1000 g $H_2O \times 10^5$	Equilibrium activity of hydroxyl ion	Equilibrium, moles aluminum/ 1000 g H_2O $\times 10^5$	$\Delta_{OH} \times 10^5$	Δ_{OH}/mole of aluminum	K
0	3.98×10^{-9}	2.97			7460.
1.04	4.17×10^{-9}	1.63			3910.
2.99	4.57×10^{-9}	1.89			4136.
12.3	1.00×10^{-8}	2.00			2000.
17.74	2.63×10^{-8}	0.78			240.
33.79	1.12×10^{-7}	0.445			40.
61.55	3.31×10^{-6}	0.667			2.02
79.28	1.62×10^{-5}	1.19	77.66	65.3	.704
95.32	4.07×10^{-5}	1.33	91.25	68.6	.327
144.9	2.09×10^{-4}	6.75	124.0	18.4	.323
295.6	8.32×10^{-4}	20.4	212.4	10.4	.245
—	1.00×10^{-3}	23.8	—	—	.240
—	1.20×10^{-3}	25.6	—	—	.210
412.4	1.48×10^{-3}	57.1	264.4	4.63	.386
1081.	5.25×10^{-3}	165.	556.0	3.4	.314
2165.	1.12×10^{-2}	227.	1045.	4.6	.202
3872.	1.41×10^{-2}	400.	2461.	6.2	.283
8440.	1.91×10^{-2}	582.	6530.	11.2	.306
30400.	—	6380.	—	—	—
60800.	—	10000.	—	—	—
91200.	—	13500.	—	—	—

Δ_{OH} = initial moles of base − equilibrium moles of base,
= base consumed by Al.

THE DATA

The data are collected in Tables I and II. The values for the activity coefficients for NaOH and $HClO_4$ are given by Robinson and Stokes (11).

From the amounts of sodium hydroxide consumed and from the ratio of consumed sodium hydroxide to dissolved aluminum, it can be concluded that a major portion of the sodium hydroxide is simply adsorbed.

TABLE II

SOLUBILITY OF ALUMINUM HYDROXIDE IN PERCHLORIC ACID SOLUTIONS OF 25° C.

Initial moles of $HClO_4$/ 1000 g H_2O $\times 10^5$	Equilibrium activity of hydrogen ion	Equilibrium, moles aluminum/ 1000 g H_2O $\times 10^5$	$\Delta_{H^+} \times 10^5$	Δ_{H^+}/mole of Al	K_1	K_2	K_3
0	2.51×10^{-6}	2.97	—	—	11.8	4.7×10^{6}	1.87×10^{12}
.81	3.55×10^{-6}	2.41	.45	.187	6.79	1.9×10^{6}	5.4×10^{11}
2.30	5.62×10^{-6}	1.52	1.74	1.145	2.70	4.8×10^{5}	8.6×10^{10}
4.58	7.94×10^{-6}	5.08	3.79	.746	6.40	8.1×10^{5}	10.2×10^{10}
5.50	9.77×10^{-6}	4.75	4.52	.952	4.86	4.97×10^{5}	50.9×10^{9}
12.67	1.55×10^{-5}	5.04	11.1	2.20	3.25	2.1×10^{5}	13.5×10^{9}
21.53	2.29×10^{-5}	6.86	19.2	2.80	2.99	1.3×10^{5}	5.72×10^{9}
25.31	2.75×10^{-5}	6.30	22.6	3.59	2.29	8.3×10^{4}	3.03×10^{9}
40.50	3.09×10^{-5}	7.42	37.4	5.04	2.40	7.8×10^{4}	2.51×10^{9}
70.88	5.01×10^{-5}	12.6	65.9	5.11	2.52	5.0×10^{4}	1.00×10^{9}
109.6	6.31×10^{-5}	31.5	103.3	3.28	4.98	7.9×10^{4}	1.25×10^{9}
181.5	8.71×10^{-5}	69.7	172.8	2.48	8.00	9.2×10^{4}	1.06×10^{9}
2380.	—	2000.	—	—	—	—	—
4680.	—	2200.	—	—	—	—	—
7000.	—	3120.	—	—	—	—	—
11700.	—	3560.	—	—	—	—	—
23400.	—	4750.	—	—	—	—	—
46800.	—	5850.	—	—	—	—	—
70400.	—	6980.	—	—	—	—	—
93000.	—	7870.	—	—	—	—	—

Δ_{H^+} = initial moles of acid − equilibrium moles of acid.

In view of the constancy of the equilibrium constant values and the relatively small amounts of solid dissolved, we believe that the following reaction is predominant in the concentrations of sodium hydroxide from 0.0008 molal to 0.08 molal.

$$Al(OH)_3\,(s) + OH^- = H_2AlO_3^- + H_2O.$$

The form $H_2AlO_3^-$, rather than $Al(OH)_4^-$, was chosen since it is felt that the equation tends to better emphasize the acid-base character of the reaction. For the equation written,

$$K = a_{H_2AlO_3^-}/a_{OH^-} = M_{H_2AlO_3^-} \cdot \gamma_{H_2AlO_3^-}/a_{OH^-}.$$

According to the Debye–Hückel limiting law, the activity coefficients for 1–1 electrolytes should be equal at equal ionic strengths; hence,

$$\gamma_{H_2AlO_3^-} = \gamma_{OH^-} = \gamma_{NaOH}$$

and

$$K = M_{H_2AlO_3^-} \cdot \gamma_{NaOH}/a_{OH^-} = 2.98\times10^{-1}$$

$$\Delta F^\circ = 720 \text{ cal/mole}.$$

Using the above equilibrium constant and K_w, the ionization constant for water at 25° C, the ionization constant for the following reaction was calculated:

$$Al(OH)_3\,(s) = H^+ + H_2AlO_3^-$$

$$K = 2.98\times10^{-15}.$$

Taking into consideration (1) the amount of acid consumed to the amount of aluminum hydroxide dissolved and (2) the fair constancy of the equilibrium constants over limited ranges of acid, we can probably conclude that in very low acid concentrations from 0 to 2×10^{-4} molal, reaction [1] below predominates and in acid concentrations from

2×10^{-4} molal to 2×10^{-3} molal, and possibly higher, reaction [3] predominates. In view of the drift in values of K_2, the range of reaction [2] cannot be determined. At most, we can only conclude that it probably occurs simultaneously with reaction [3] in the intermediate concentration of acid near 2×10^{-4} molal.

$$Al(OH)_3\,(s) + H^+ = Al(OH)_2^+ + H_2O \qquad [1]$$

$$Al(OH)_3\,(s) + 2H^+ = Al(OH)^{+2} + 2H_2O \qquad [2]$$

$$Al(OH)_3\,(s) + 3H^+ = Al^{+3} + 3H_2O \qquad [3]$$

$$K_1 = a_{Al(OH)_2^+}/a_{H^+} = M_{Al(OH)_2^+}\cdot\gamma_{Al(OH)_2^+}/a_{H^+}.$$

As before,

$$\gamma_{Al(OH)_2^+} = \gamma_{HClO_4}$$

and

$$K_1 = M_{Al(OH)_2^+}\cdot\gamma_{HClO_4}/a_{H^+} = 2.52$$

$$\Delta F_1^\circ = -550 \text{ cal/mole.}$$

Since K_2 was not constant, no attempt was made to select a representative value for it.

$$K_3 = a_{Al^{+3}}/a_{H^+}^3 = M_{Al^{+3}}\cdot\gamma_{Al^{+3}}/a_{H^+}^3.$$

From the Debye–Hückel limiting law, the activity coefficient of a 1–3 electrolyte may be replaced by the cube of that for a 1–1 electrolyte; hence,

$$K_3 = M_{Al^{+3}}\cdot\gamma_{HClO_4}^3/a_{H^+}^3 = 1.10\times10^9$$

$$\Delta F_3^\circ = -12{,}300 \text{ cal/mole.}$$

Using the value obtained for K_3 above and the cube of K_w, the ionization constant for water at 25° C, the solubility product constant for the following reaction was calculated:

$$Al(OH)_3\,(s) = Al^{+3} + 3OH^-,$$

$$K = 1.10\times10^{-33}.$$

For an amphoteric hydroxide, the isoelectric point will represent the minimum solubility. Plotting the logarithm of the reciprocal of the solubility against pH gives a curve with a maximum at pH 7.7.

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A STUDY OF SILVER NITRATE SOLUTIONS IN GAS CHROMATOGRAPHY[1]

M. E. Bednas and D. S. Russell

ABSTRACT

Silver nitrate, dissolved in some organic solvents, has formed a relatively specific medium for the gas chromatographic separation of olefins. Columns formed from ethylene glycol and glycerin solutions of silver nitrate are comparable, but those formed from the polyethylene glycol solutions are considerably less effective. These silver nitrate solutions were stable below 65° C, but began to decompose slowly at 85° C.

An aspect of gas chromatography which has received little attention in the literature has been the use of liquid phases which react with components of the sample to form unstable complexes. A solution of silver nitrate in ethylene glycol has been used to form a column of this type. It is relatively specific for olefins, retaining ethylene and propylene, for example, much longer than such higher-boiling paraffins as *n*-pentane and *n*-hexane.

The existence of unstable complexes of this type has been demonstrated by Francis (1), who isolated a compound from propylene and silver nitrate. This proved to be stable at room temperature and normal pressure, but decomposed reversibly to silver nitrate and propylene at reduced pressures or at higher temperatures. The use of silver nitrate in a gas chromatographic column was first reported by Bradford *et al.* (2). They found that a saturated solution of silver nitrate in ethylene glycol on a support of kieselguhr gave excellent separations for traces of ethane in ethylene. Tenney (3) has clearly illustrated the selective effect of silver nitrate for normal olefins from pentene-1 through to nonene-1.

The moisture which is sometimes present in ethylene glycol and similar solvents, or that which these solvents absorb from samples containing traces of water, is subsequently eluted during the chromatographic process and frequently interferes with the determination. To circumvent this problem van de Craats (4) has suggested the use of benzyl cyanide as a solvent for silver nitrate, but has not included any data on this column.

The papers referred to above have not considered the temperature stability of these columns. Keulemans (5) states that the temperature should be kept below 40° C, since above this temperature the transient adducts with silver nitrate are not formed, and the solution is not stable.

This present study was undertaken to pursue this temperature stability further and to obtain comparative results for columns of ethylene glycol, polyethylene glycol, and glycerin solutions of silver nitrate.

EXPERIMENTAL

Apparatus

A commercial chromatographic unit, the Fisher-Gulf Partitioner, was employed. The columns consisted of $\frac{1}{4}$-inch copper tubing wound into a coil 6 inches in diameter. A thermistor serves as a detector. Both the detector and the column are contained in

[1]*Manuscript received May 22, 1958.*
Contribution from the Division of Applied Chemistry, National Research Council of Canada, Ottawa, Canada. Issued as N.R.C. No. 4843.

the same air bath, which can be controlled at the following steps, 50°, 65°, 85°, 100°, 120°, and 140° C. It can also be used at its ambient temperature (27° C) but without control. In this case the drift was less than 1% of full scale deflection at full sensitivity over a period of 20 minutes. The peaks are recorded on a conventional strip-chart recorder, fitted with a ball-and-disk integrator.

In these experiments helium was the only carrier gas used.

Reagents

Silver nitrate, Mallinckrodt Analytical Reagent.
Ethylene glycol, Eimer and Amend.
Triethylene glycol (mol. wt. 200), Carbide and Carbon, "Carbowax".
Polyethylene glycol (mol. wt. 400), Carbide and Carbon, "Carbowax".
Glycerin, Baker and Adamson.

Preparation of Columns

Approximately 30 g finely pulverized silver nitrate was added slowly to 20 ml glycerin (or glycol) in a beaker while stirring vigorously with a magnetic stirrer. In some cases the beaker was placed in warm water to hasten the solution of the salt. Care was taken to keep the temperature below 50° C. After several minutes stirring the undissolved silver nitrate was separated by centrifuging for a few minutes.

Exactly 17 ml of this saturated solution was then added to 39 g (100 ml) 30–60 mesh firebrick to give a packing which contained about 40% solvent by weight. The usual care was taken to ensure a uniform mixture. The resulting material appeared to be quite dry and flowed readily.

Sufficient ¼-inch diameter copper tubing was degreased and filled with the prepared packing. Approximately 6 ml of packing was required to fill 1 foot of tubing. The tubing was carefully filled while it was suspended by one end, being shaken at intervals to produce a uniform bed. The ends were plugged with glass wool and the tubing was wound to form a coil 6 inches in diameter.

RESULTS

Columns were prepared as described containing relatively saturated solutions of silver nitrate in ethylene glycol, polyethylene glycol, and glycerin. The relative retention times

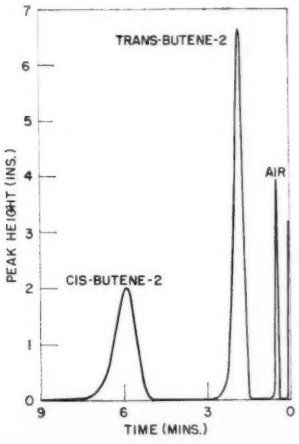

FIG. 1. Separation of *cis*- and *trans*-butene-2.

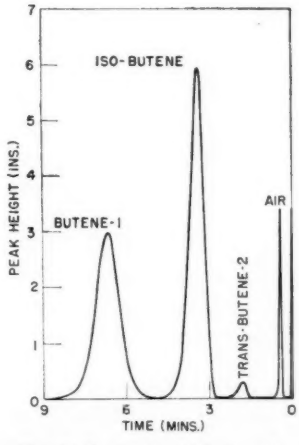

FIG. 2. Separation of butene-1 and isobutene.

which were obtained from the solutions of ethylene glycol and glycerin are given in Tables I and II. It will be observed that the *cis*- and *trans*-butene-2 are well separated as are the isobutene and the butene-1. These two pairs have been difficult to resolve with most other columns (2, 6, 7, 8, 9, 10). Their chromatograms are shown in Figs. 1 and 2.

TABLE I

RELATIVE RETENTION TIMES FOR $AgNO_3$ – ETHYLENE GLYCOL COLUMN

11-ft column
50° C
Flow rate, 25 ml/minute
Corrected retention time for ethylene, 4.5 minutes

	Retention time (ethylene = 1.00)	
n-Pentane (and lighter alkanes)	0	(Not retained)
trans-Butene-2	0.56	
trans-Pentene-2	0.89	
Ethylene	1.00	
Isobutene	1.19	
Propylene	1.22	
cis-Butene-2	2.0	
Butene-1	2.35	
Pentene-1	2.8	
cis-Pentene-2	2.95	
Hexene-1	4.2	
Heptene-1	6.1	
Octene-1	8.9	

TABLE II

RELATIVE RETENTION TIMES FOR $AgNO_3$ – GLYCERIN COLUMN

11-ft column
50° C
Flow rate, 20 ml/minute
Corrected retention time for ethylene, 4.5 minutes

	Retention time (ethylene = 1.00)	
n-Pentane (and lighter alkanes)	0	(Not retained)
trans-Butene-2	0.31	
Isobutene	0.75	
Propylene	0.91	
Ethylene	1.00	
cis-Butene-2	1.17	
Pentene-1	1.32	
Butene-1	1.42	
Ethylene dichloride	3.3	
Butadiene	6.0	
Cyclopentene	9.8	
Isopropanol	40.	
n-Propanol	60.	

The retention time for *cis*-butene-2 relative to that of *trans*-butene-2 is given in Table III for the three columns. The proportion of the silver nitrate on the firebrick is also given to demonstrate the relation between the silver nitrate concentration and the efficiency of the separation. This relation was also borne out when more dilute solutions were used and again when some of the silver nitrate was found to be decomposed in the column. With columns containing no silver nitrate (or those in which the silver nitrate was completely reduced), all olefins and paraffins containing four carbon atoms or less were not retained at all (i.e. not separated from air).

TABLE III

SELECTIVITY FOR *cis*- AND *trans*-BUTENE-2

Column	Column length, ft	% $AgNO_3$ on fire-brick	Ratio *cis/trans* 27° C	Ratio *cis/trans* 50° C		
1. $AgNO_3$ – ethylene glycol	11	24.	4.1	3.6		
2. $AgNO_3$ – polyethylene glycol	11	8.3	—	1.8		
3. $AgNO_3$ – glycerin	11	24.	4.7	4.1		
4. Formamide	6				1.18	(0° C)
5. Dimethylsulpholane	50	(⅜ inch diam.)			1.17	(0° C)
6. Alumina	7				1.21	(60° C)
7. Tri-isobutylene	6				0.90	
8. Acetonyl acetone	6				0.86	(20° C)
9. $AgNO_3$ – ethylene glycol	6				0.32	
10. $AgNO_3$ – ethylene glycol ($AgNO_3$ completely decomposed)	11	*cis*- and *trans*-Butene-2 not retained				
11. Ethylene glycol	11	*cis*- and *trans*-Butene-2 not retained				

The concentration of silver nitrate found in solutions prepared as described is given in Table IV and may be regarded as relatively saturated solutions at room temperature.

TABLE IV

SOLUBILITY OF $AgNO_3$

Glycerin	95	g/100 ml	solution
Ethylene glycol	85	,,	,,
Triethylene glycol (mol. wt. 200)	48	,,	,,
Polyethylene glycol (mol. wt. 400)	32	,,	,,

The *cis–trans* ratios of five other columns are also included in Table III, columns 4–9, as calculated from results reported by other workers. The values reported by Bradford *et al.* (2), columns 7, 8, 9, gave ratios which were less than unity and indicate that the *cis*-butene-2 was eluted before the *trans*-butene-2. Our observations in the case of the silver nitrate – ethylene glycol column have not confirmed this fact. If, however, the values for *cis* and *trans* are interchanged in Bradford's report a *cis–trans* ratio of 3.1:1 is obtained, which is in agreement with the authors' findings.

The authors have employed "two-stage" columns (8) in an attempt to separate paraffins as well as olefins on one column. This consisted of a silver nitrate – glycerin column for separating the olefins, in series with a dinonyl phthalate column for separating the paraffins. Little success was achieved.

As an alternative, we suggest that a silver nitrate – glycerin column be employed for analysis of the olefins, and the paraffin fraction collected for subsequent analysis on a dinonyl phthalate or similar column.

Stability of Silver Nitrate Columns

The instability of the silver nitrate solutions seriously limits the use of the column to lower temperatures. It was therefore considered desirable to obtain further information concerning the temperature at which the decomposition begins, and its rate. Glycerin was also compared as a solvent in the hope that it might prove superior to ethylene glycol.

An ethylene glycol – silver nitrate column was heated to 100° C for 16 hours, and then tested for its efficiency at 35° C. No appreciable separation of *cis*- and *trans*-isomers took place, although the same column had previously shown a *cis–trans* ratio of 3.6:1

(column 1, Table III). The packing was recovered from the column and the organic phase was diluted with water. Upon titration with chloride this solution indicated the presence of little or no silver ion. The original titration for silver was obtained, however, if the packing was first digested with dilute nitric acid. From the examination of similar columns, it was found that the efficiency of the column was directly related to the concentration of silver ions present.

Ethylene glycol – silver nitrate and glycerin – silver nitrate packings were prepared on firebrick as described and kept in closed bottles. These bottles were stored in a controlled oven for periods of several days, when small samples were removed and titrated with chloride. The results which were obtained are illustrated in Fig. 3.

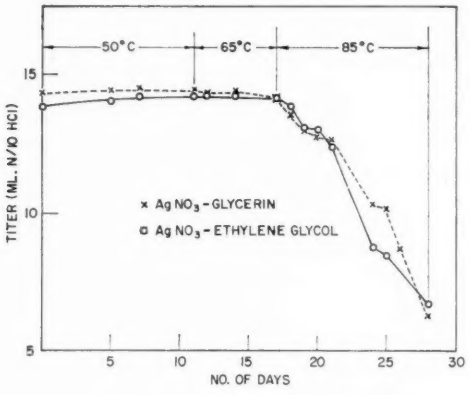

FIG. 3. Thermal stability of columns.

Both column materials were stable at least up to 65° C but decomposed slowly at 85° C. Subsequently a silver nitrate – ethylene glycol column has shown no change in relative retention times after 12 days at 65° C. It has been used intermittently at various temperatures not exceeding 65° C for 6 months, with no significant change in the relative retention times.

CONCLUSIONS

It may be concluded that the ethylene glycol and glycerin columns may be used safely up to 65° C and even at 85° C for short periods without serious damage. The glycerin – silver nitrate column had no distinct advantages, although it did show slightly better separations than its ethylene glycol counterpart. Polyethylene glycol proved less suitable probably owing to its more limited solubility of silver nitrate.

One noteworthy characteristic of these columns is their use for separating the paraffins as a group from the olefins.

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THE LIMITING CONDUCTANCE OF POTASSIUM IODATE AND OF IODATE ION AT 25.00° C[1]

A. N. Campbell and E. Bock[2]

ABSTRACT

Measurements have been made of the equivalent conductance of solutions of potassium iodate, at 25.00° C, at concentrations ranging from 0.8×10^{-4} to 16×10^{-4} *N*. From this the limiting equivalent conductance of potassium iodate is found to be 114.41 mhos and that of iodate ion 40.91 mhos. The experimental technique is described. The ionic conductances of chlorate, bromate, and iodate ions are compared.

INTRODUCTION

We are beginning, in this laboratory, an investigation of the conductances of very dilute solutions at temperatures above 25.00° C, in order to know the limiting conductances, both equivalent and ionic, above 25° C. This again has a bearing on our work on concentrated solutions, which has been appearing over the last 8 years (1, 2, 3, 4, 5, 6, 7, 8). We have already published one paper on the limiting conductances of ammonium chloride, ammonium bromide, and ammonium nitrate, at 35.00° C (9). Since then, however, we have refined our techniques and we intend this paper to be a statement of the experimental method to be used throughout the series, although, of course, as the temperature of measurement is raised further precautions will have to be taken to obtain constancy of temperature, to prevent distillation or even boiling, etc.

As a preliminary exercise, we have determined the limiting conductance of potassium iodate and of iodate ion, at 25.00° C. Apart from three rather early measurements by Harkins and Pearce (10) nothing has been done on iodate ion, although the limiting conductances of chlorate and bromate, at 25° C, have been determined with great accuracy (11, 12).

EXPERIMENTAL PROCEDURE

The electrical circuit for work of this kind is now standard. We are indebted to the International Nickel Company and to the Imperial Oil Company for the provision of a Jones bridge. The signal is amplified by a tuned amplifier. The detector is a cathode ray oscillograph; it is thus possible to differentiate between resistance and capacity imbalance. Measurements were made at the standard frequency of 1000 but measurements were also made at other frequencies to show that the apparent resistance did not vary with the frequency, as it should not if the true resistance is being measured.

Our conductance cell, of silica, is identical with that used by Shedlovsky (13). The thermostat is a double-jacketed, completely enclosed oil bath, containing 16 gal of mineral oil; the air over the bath is stirred and heated to a temperature slightly above that of the bath. Temperature is determined by a platinum resistance thermometer, and Mueller bridge.

The thermometer was obtained from the National Research Council and calibrated by them. We use a large toluene mercury regulator and thyatron control (14). The variation of temperature does not exceed 5×10^{-3} ° C. The potassium iodate was a Fisher certified reagent of the very highest purity and we felt that nothing would be gained by an additional recrystallization. Moreover, as the impurities in the salt—less than 0.01% in total—were ionic in nature, the error introduced into the conductance value

[1]*Manuscript received June 12, 1958.*
Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Manitoba.
[2]*Holder of a C.I.L. Fellowship, 1957–58.*

will be proportional to the difference in conductance of the salt investigated and the impurities; an error a great deal less than 0.01%. The salt was dried at 150° C and kept over P_2O_5 in a desiccator until needed. As for conductance water, we began by using an ion-exchange column, employing MB-3 (Fisher) ion-exchange resin. We found, however, that, although the issuing water had a very low conductance at first (2×10^{-7} mhos), this increased with time. It appears that something is extracted from the material of the column which subseqently undergoes chemical change with production of an electrolyte. The increase in conductance is small but, since the water conductance correction is considerable (about 10% of the whole for the most dilute solution used) in these very dilute solutions, it must be constant and known with accuracy. We therefore simply use the water from an electric still, from which we remove dissolved gases with bubbling nitrogen. This water has a conductance of 4.5×10^{-7} to 7×10^{-7} and it does not change with time, when preserved in a silica container. The conductance cell was subjected to a prolonged steaming operation until we were convinced, from experimental measurement, that the conductance of water stored in it did not change with time. All measurements are carried out in an atmosphere of nitrogen.

The balance used is a single-pan semimicro type, having a sensitivity of 0.01 mg. Since we do not possess a microbalance, it is not possible to make up the most dilute solutions by introducing the very small weights of dry salt directly into the cell. We have therefore used a weight burette for the purpose of obtaining a solution of known concentration. The cell constant was determined in the usual way with 1/100 demal potassium chloride. As a final test of technique, we determined some of the conductances of potassium chloride at 25.0° C (at various concentrations) and we obtained exact agreement with the results of Shedlovsky and of Gordon (13, 15).

The only previous work on potassium iodate at 25.00° C is that of Harkins and Pearce (10), who report the conductances at three rounded-off concentrations, viz., 0.2×10^{-3}, 0.5×10^{-3}, and 1×10^{-3}. From these figures, they state the limiting conductance to be 114.37 mhos, in close agreement with our figure but we do not see what justification they can have for this, since they presumably (no details are given) only made three determinations plotted. And then, again presumably, they plotted Λ versus $\sqrt{c}$, and drew a straight line, more or less at random, through the three points. Yet when such a plot is constructed the extrapolated value of Λ_0 comes to 114.20 mhos.

EXPERIMENTAL RESULTS

Our results are contained in the following table.

TABLE I

THE SPECIFIC AND EQUIVALENT CONDUCTANCES OF AQUEOUS SOLUTIONS OF POTASSIUM IODATE AT 25.00° C

Concentration, in moles/liter $\times10^4$	Specific conductance $\times10^6$, in mhos	Equivalent conductance, in mhos
0.86082	9.78064	113.62
2.05973	23.30996	113.17
3.14043	35.45545	112.90
4.69655	52.85967	112.55
6.58631	73.90498	112.21
8.66525	96.93815	111.87
10.81886	120.72765	111.59
12.92765	143.92353	111.33
14.11540	157.96544	111.19
15.64277	173.66603	111.02
16.88694	187.24239	110.88

When the above results are plotted in the form of Λ versus $\sqrt{c}$, and the best straight line drawn (by the method of least squares), it is seen that no single determination deviates from the line by more than 1/100%. The slope of the line (85.91) is very close to the theoretical Debye–Hückel slope (86.51) but is somewhat less; this is what is usually found. When the line is extrapolated to zero concentration, Λ_0 results as 114.41. Taking the limiting conductance of potassium ion to be 73.50 (15, 16) at 25.00° C, the limiting conductance of iodate ion results as 40.91.

DISCUSSION

Since the limiting conductances of chlorate, bromate, and iodate ions are now known with accuracy, there is some interest in comparing them with the dimensions of the crystallographic ions (17), thus:

TABLE II

COMPARISON OF LIMITING IONIC CONDUCTANCES WITH DIMENSIONS OF CRYSTALLOGRAPHIC IONS

Ion	Limiting conductance	Edgelength of tetrahedral ion
ClO_3^-	64.6	2.33 Å
BrO_3^-	55.74	2.73 Å
IO_3^-	40.91	3.35 Å

The ratio of conductances is 1.58:1.36:1 and that of edgelength 1.44:1:1.71 iodate, with the largest (crystallographic) ion size, has the smallest ionic conductance, but the agreement is obviously not quantitative. Indeed, similar calculations with other ions (notably the bromide ion) show that sometimes an ion may even have a greater apparent size and yet have a greater conductance. It is well known that Stokes' law does not apply to the motion of particles as small as the smaller ions. Stokes and Robinson (18) consider the problem of how large an ion must be in order that Stokes' law may be obeyed and assign a lower limit. Nevertheless though quantitative agreement with Stokes' law is not to be expected here, if the crystallographic dimensions were true measures of the sizes of the ions in solution qualitative agreement should exist.

Differences in solvation may account for the discrepancy although other explanations are possible.

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DIACETYLENE: PREPARATION, PURIFICATION, AND ULTRAVIOLET SPECTRUM[1]

K. K. Georgieff and Y. Richard

ABSTRACT

Diacetylene was prepared by the reaction of 1,4-dichloro-2-butyne with sodium hydroxide. Three modifications of procedure were tried to determine which gave the highest yield and purest product. Evidence that the by-product is 2-chloro-2-butene-3-yne is presented. Several methods for purifying the diacetylene were investigated. The ultraviolet spectrum with molar extinction coefficients is given.

INTRODUCTION

A sample of very pure diacetylene was required for polymerization and spectroscopic studies. In recent years most investigators have prepared it by the dehydrochlorination of 1,4-dichloro-2-butyne with sodium hydroxide (1, 2, 3, 4, 5) but only one (4) appears to have reported that the product is not entirely pure. However, no indication of the nature of the impurity was given.

RESULTS

Several modifications of the dehydrochlorination were tried to determine which gave the highest yield and purest product. The yields were highest when 40% aqueous sodium hydroxide solution (285% of theory) was added to a 25% solution of 1,4-dichloro-2-butyne[2] in ethyl alcohol at 65–75° over a period of 1 hour (1) and the product was swept out of the reaction flask with a stream of hydrogen. However, a small percentage of a by-product having a parent peak of 86 in its mass spectrum, as well as tarry high polymers, also formed. When the procedure was reversed and the dichlorobutyne in alcohol was added to the sodium hydroxide, the yield of diacetylene was substantially lower and the fractionated product contained about the same concentration of the same impurity. When pure dichlorobutyne was added to 43% sodium hydroxide solution at 115°, the yield was still lower but the relative amount of the above impurity was lower. Some acetylene and methyl acetylene also formed and were detected by their mass spectra.

From the ratio of the 87 to the 86 mass peak, the spectrum indicates that the impurity contains four carbon atoms and the ratio of the 86 to the 88 peak is in good agreement with the known ratio of Cl_{35} to Cl_{37}. It would thus appear that its empirical formula is C_4H_3Cl. It also has a strong absorption at 224 to 245 mμ in the ultraviolet and its extinction coefficients are of a higher order than those of diacetylene, indicating two conjugated ethylenic groups or an ethylenic together with an acetylenic. From the above evidence, there would appear to be little doubt that this compound formed, even in the presence of a large excess of sodium hydroxide, by the incomplete dehydrochlorination of the dichlorobutyne and could theoretically have the structure I, II, or III.

$$CH_2Cl—C\equiv C—CH_2Cl + NaOH \rightarrow NaCl + H_2O + CH_2{=}CCl—C\equiv CH \quad [I]$$

$$\text{or } CHCl{=}CH—C\equiv CH \quad [II]$$

$$\text{or } CH_2{=}CH—C\equiv C—Cl \quad [III]$$

To establish its identity, its infrared spectrum was obtained and a comparison made of the out-of-plane vibrations of its olefinic hydrogens with those of four compounds

[1]*Manuscript received June 3, 1958.*
Contribution from the Research Laboratories, Shawinigan Chemicals Ltd., Shawinigan, Que.
[2]*Available from General Aniline & Film Corporation, U.S.A.*

closely related with I, II, and III, as shown in Table I. The band assignments previously published for monovinylacetylene (6, 7, 8) and 2-chloro-1,3-butadiene (9, 10) were assumed. Since only a fragmentary spectrum for 1-chloropropene-1 appears to have been previously published (10), it was first necessary to obtain samples of 1- and 2-chloropropene-1 (from K. & K. Laboratories, U.S.A.) and purify them by distillation in a Podbielniak column. Their purity was checked with the mass spectrometer.

TABLE I

ASSIGNMENT OF INFRARED BANDS (cm^{-1})

Out-of-plane vibrations of olefinic hydrogens	CH_3—CH=CHCl	CH_3—CCl=CH_2	CH_2=CH—CCl=CH_2	CH_2=CH—C≡CH	Our impurity
CH_2=CH—			974 (9, 10) 924	972 (8) 924	
CH_2=CCl—		938 929			919 862
		881	878		853
R—CH=CHX (*trans*)	932				
R—CH=CHX (*cis*)	766 754				

Our impurity showed a band of medium intensity at 919 cm^{-1} and a strong doublet at 862 and 853 cm^{-1}. Both 2-chloro-1,3-butadiene and 2-chloropropene-1 show absorptions in the same regions whereas 1-chloropropene-1 shows absorption at 932 and a doublet at 766 and 754 cm^{-1}, which, in accordance with the correlations established by Kitson (10), could be attributed to *cis*- and *trans*-isomers. There is little spectral evidence in support of structure III. Neither is it probable on chemical grounds. It would thus appear that the structure of our impurity is I, CH_2=CCl—C≡CH. The shift of the chlorine atom from the 1-carbon to the 2-position is reminiscent of that of chlorobutadiene (11).

PURIFICATION

Attempts to remove the 2-chloro-2-butene-3-yne by the high vacuum, fractional distillation – condensation technique (8, 12) using distilling temperatures from −60 to −95° failed. So did distillation from solvents such as ethyl acetoacetate and methyl isobutyl ketone, as well as conventional, simple distillation at 277 mm mercury absolute. Fractional recrystallization was abandoned owing to great experimental difficulties imposed by the necessity of keeping the sample very cold and away from oxygen. Attempts to remove the impurity by partially polymerizing the sample at −6 to +13° in the absence of air and catalyst increased its concentration, thus indicating that the diacetylene polymerized more rapidly. Diluting the diacetylene with 10 to 15 volumes of hydrogen and passing it rapidly through a solution of sodium hydroxide in amyl alcohol at 138° reduced the chloro impurity from 1.5 to 0.2% but only 10–20% of the diacetylene was recovered. The remainder polymerized to tar. Gas chromatography, on the other hand, was found to produce high purity diacetylene with high recoveries. A tube (20 ft long × $\frac{1}{4}$ inch O.D.) filled with Johns-Manville C-22 firebrick (35–50 mesh) which was impregnated with 33% tricresyl phosphate was employed. Using a diacetylene vapor sample of about 5 ml (measured at 760 mm), a hydrogen flow of 67 ml per minute, and a tube temperature of 65°, the recovery was at least 93% per pass. After one or two passages through the tube, no 2-chloro-2-butene-3-yne could be detected by the mass spectrometer.

It is well known that the loss of diacetylene is substantial if it is handled by the usual laboratory techniques owing to its volatility and ease of polymerization. However, it was found that by using the high-vacuum, low-temperature-distillation technique (8, 12), such loss was reduced to a negligible value. By storing the samples (whether pure or impure) at -50 to $-78°$ under vacuum, losses due to polymerization were very small, even after 1 year without a stabilizer. The preferred procedure was to distill the diacetylene into a glass tube, cool it with liquid nitrogen, evacuate to a pressure of at least 10^{-4} mm mercury, and seal the tube. However, when the sample contained dissolved gas (usually air), it was first necessary to degas it several times by successively warming it to -20 to $0°$, cooling with liquid nitrogen, and pumping off the gas.

ULTRAVIOLET SPECTRUM

The ultraviolet spectrum of diacetylene vapor has been published by Price and Walsh (13) for the 1000 to 2000 Å region and by Woo and Chu (14, 15, 16) for the 2068 to 2970 Å region. Our spectrum was obtained with a Beckman DK-2 spectrophotometer on samples dissolved in iso-octane. There was general agreement with Woo and Chu's spectrum but there was a shift in our peaks of 7 to 9 mμ towards the lower wave lengths and some differences in the relative intensities of the maxima were apparent. The curve is given in Fig. 1 and the molar extinction coefficients in Table II. Our values are of the same order of magnitude as those obtained by Armitage *et al.* (17) on substituted diacetylenes.

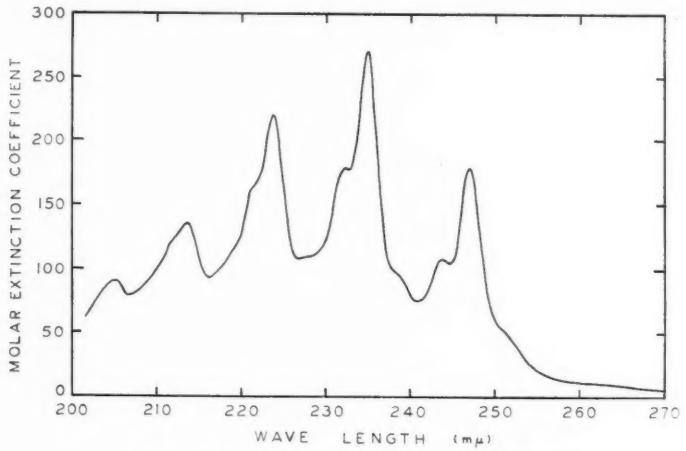

FIG. 1. Ultraviolet spectrum of diacetylene in iso-octane.

TABLE II

ULTRAVIOLET SPECTRUM OF DIACETYLENE

CONCN. = 7 TO 30 $\times 10^{-4}$ MOLES PER LITER IN ISO-OCTANE

λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
~205	~90	223.8	222	244	110
211.3sh	117	232.5	180	247.1	180
213.5	136	234.9	270	251.5	55
221.5sh	168	238.5	101		

Extinction values were also obtained on a Beckman DU instrument and were generally 10 to 20% lower than those above. In contrast to those obtained with the DK-2, they were found to decrease rapidly with increase in concentration of diacetylene even at low optical densities (i.e. 0.1 to 0.3). A similarly great deviation from the Beer–Lambert–Bouger absorption law was noted previously with monovinylacetylene and other acetylene polymers (8).

ACKNOWLEDGMENTS

The authors wish to express their thanks to Shawinigan Chemicals Ltd. for permission to publish this paper and to Messrs. A. Dupré, E. Blais, and E. Beaulieu for their assistance.

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SOME CHEMISTRY OF 2,6-DIETHYLANILINE[1]

P. M. G. BAVIN[2] AND J. M. W. SCOTT[3]

ABSTRACT

Orientation in the nitration and bromination of amides derived from 2,6-diethylaniline has been shown to be dependent on the acidity of the reaction medium, as found previously for the 2,6-dimethyl homologues.

The acidity of the reaction medium is known to influence the orientation of substitution products of many amines (1, 2, 3, 4, 5, 6, 7) and their derivatives, particularly anilides and sulphonamides (8, 9, 10, 11). Derivatives of 2,6-dimethylaniline (*m*-2-xylidine) have proved to be of more than usual interest (9, 10), so that the opportunity has been taken to examine some of the chemistry of 2,6-diethylaniline.

2,6-Diethylaniline was recently prepared for the first time (12). It forms nicely crystalline salts with hydrochloric, hydrobromic, and perchloric acids which, as expected for the salts of weak bases (13), are partly hydrolyzed in water. With benzaldehyde it reacts smoothly to form a Schiff's base and readily forms amides with acetic anhydride, benzoyl chloride, and *p*-toluenesulphonyl chloride. The acetamide (X) is very resistant to acid hydrolysis so that the toluenesulphonamide (I) was preferred as an intermediate.

Nitration of (I) in the presence of nitrous acid (7, 10) gave an excellent yield of pure 4-nitro derivative (II), the structure of which was proved by conversion to the known 4-nitro-2,6-diethylphenol (IV) and 2,6-diethyl-1,4-benzoquinone (V). In sulphuric acid, nitration gave a rather lower yield of the 3-nitro derivative (VI), its structure being assumed by elimination. The acetamide (X) readily yielded a dinitro compound, almost certainly (VII), and considerable difficulty was encountered in obtaining the 3-nitro derivative (VIII).

Bromination of the acetamide (X) in sulphuric acid gave the 3-bromo derivative (IX), the structure of which is assumed by analogy with previous work on the dimethyl homologue (9). In acetic acid or chloroform, the 4-isomer (XII) was obtained. This compound, the structure of which is also assumed by analogy (9), has been shown to be formed by the rearrangement of the *N*-bromoacetamide (14). Bromination of the sulphonamide (I) in sulphuric acid, chloroform, or acetic acid gave products which were not obtained pure by repeated crystallization and whose infrared spectra showed them to be essentially identical. Removal of the tosyl group followed by acetylation gave almost pure (XII), showing that bromination had occurred predominantly in the 4 position.

Aniline, the toluidines, and related compounds are very much more reactive than their salts so that the small concentration of free amine present in sulphuric acid largely controls the orientation in nitration in this medium (1, 2, 3, 4, 5, 6, 7). Derivatives of 2,6-dialkylaniline (alkyl is methyl or ethyl) offer a more complex problem. The proximity of the ortho substituents twists the amide group out of the plane of the aromatic ring,* thereby greatly reducing mesomerism between the ring and the nitrogen (10, 15, 16).

[1]*Manuscript received April 8, 1958.*
Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada, and the Divisions of Pure and Applied Chemistry, National Research Council, Ottawa.
Issued as N.R.C. No. 4801.

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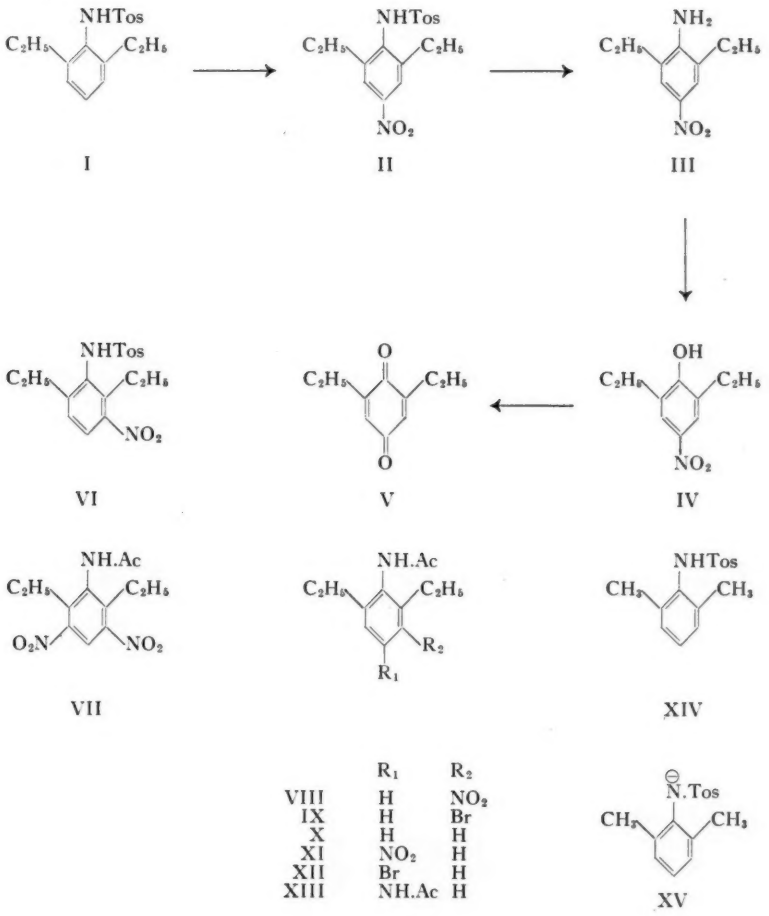
**Reducing mesomerism between the ring and the nitrogen will increase the basicity of the latter, but the compression caused by the ortho substituents may nullify or even out-balance this effect ((17), pp. 214–223).*



I II III IV V VI VII XIV XV

	R_1	R_2
VIII	H	NO_2
IX	H	Br
X	H	H
XI	NO_2	H
XII	Br	H
XIII	NH.Ac	H

This lowers the reactivity of the 4 position but leaves it more reactive than the 3 position (10). Since in sulphuric acid 3-derivatives are usually obtained, it appears that the protonated and unprotonated forms differ but little in reactivity at the 3 position.

The sulphonamides (I) and (XIV) and their *N*-nitroso derivatives are probably insufficiently reactive to undergo nitrosation (cf. (7)) so that (XV) has been suggested (10) as the reactive species in nitration in the presence of nitrous acid.

As expected, nitration of (I) and bromination of (X) are completely analogous to reactions of the dimethyl homologues (9, 10). That bromination of (I) in sulphuric acid gives rise to predominantly the 4-isomer may be due to the low basicity of the sulphonamide group and the greater selectivity of bromination compared with nitration (18).

It was hoped initially to confirm the structures of the bromination products by comparison of their infrared spectra with those of the corresponding nitro compounds. This hope was not realized, only approximate similarities being observed.

EXPERIMENTAL

2,6-Diethylaniline was supplied as a reddish liquid and used without purification.

Melting points are uncorrected. Most of the nitration products turned brown in light and were crystallized in covered flasks. Nitration conditions were essentially those used by Wepster for the dimethyl homologues (10).

2,6-Diethylaniline hydrochloride crystallized from dilute hydrochloric acid as colorless needles, m.p. 175–179° with decomposition. Calc. for $C_{10}H_{16}NCl$: C, 64.68; H, 8.69%. Found: C, 64.48; H, 8.44%. Crystalline salts were also formed with perchloric and hydrobromic acids but these were not characterized. The free amine separated as an oil when the salts were dissolved in warm water.

N-Benzal-2,6-diethylaniline.—On the gentle warming of a mixture of the amine (2 g.) with benzaldehyde (4 g.), water started to separate almost at once. Ethanol (2 ml.) was added and the mixture boiled under reflux for 10 minutes. The Schiff's base was obtained as a pale yellow solid by pouring the mixture into an excess of cold dilute sodium bisulphite solution. Two crystallizations from hexane afforded yellow prismatic needles (2.6 g.), m.p. 54–55°. Calc. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90%. Found: C, 86.20; H, 8.08; N, 5.88%.

N-(2,6-Diethylphenyl)-benzamide was prepared by shaking the amine (2 g.) with benzoylchloride (3 ml.) and a solution of sodium hydroxide (5 g.) in water (10 ml.). The solid product was crystallized twice from toluene, affording slender needles (2.2 g.), m.p. 236–237°. Calc. for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53%. Found: C, 80.73; H, 7.42; N, 5.66%.

N-(2,6-Diethylphenyl)-acetamide (X) was prepared by adding acetic anhydride (200 ml.) dropwise to the amine (100 g.) cooled in an ice bath. The reaction, which was rapid and exothermic, was completed on the steam bath. Addition of 10% sulphuric acid (500 ml.) and crushed ice precipitated the amide. Crystallization from ethanol (200 ml.) afforded white needles (110 g.), m.p. 139–140°, raised to 141–142° by two crystallizations from toluene. (Lit. m.p. 135–136°, (12).) Calc. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32%. Found: C, 75.56; H, 8.71; N, 7.46%.

N-(2,6-Diethylphenyl)-p-toluenesulphonamide (I).—The amine (150 g.) was dissolved in dry pyridine (500 ml.) and *p*-toluenesulphonyl chloride (210 g.) added slowly while the mixture was cooled with an ice–salt bath. Next morning, the mixture was poured onto crushed ice and the pyridine neutralized with dilute hydrochloric acid. Crystallization from methanol–acetone (Norite) afforded yellowish prisms (265 g.), m.p. 130–132°. An analytical sample was obtained as well-defined colorless prisms, m.p. 132–133°, after two crystallizations from benzene. Calc. for $C_{17}H_{21}NO_2S$: C, 67.31; H, 6.98; N, 4.62%. Found: C, 67.45; H, 6.98; N, 4.49%.

N-(4-Nitro-2,6-diethylphenyl)-p-toluenesulphonamide (II).—A mixture of the amide (I) (30 g.), acetic acid (100 ml.), fuming nitric acid (40 ml.), and sodium nitrite (2 g.) was boiled under reflux for 1 hour. Pouring onto ice precipitated a gum which soon crystallized. Successive crystallizations from methanol (Norite) and benzene–hexane afforded the nitroamide as pale yellow needles (22–25 g.), m.p. 140–141°. Calc. for $C_{17}H_{20}N_2O_4S$: N, 8.04%. Found: N, 8.18%.

4-Nitro-2,6-diethylaniline (III).—The nitroamide (II) (10 g.) was stirred overnight with sulphuric acid (30 ml.) containing water (4 ml.). Pouring onto ice precipitated the pale yellow amine sulphate, which was decomposed to the amine by neutralization with dilute ammonia solution. Two crystallizations from methanol gave long bright yellow needles of the amine, m.p. 137–138°. Calc. for $C_{10}H_{14}N_2O_2$: N, 14.42%. Found: N, 14.59%.

N-(4-Nitro-2,6-diethylphenyl)-acetamide (XI) was prepared by acetylating the amine (III). It crystallized from benzene–hexane as pale yellow needles, m.p. 195–196°. Calc. for $C_{12}H_{16}N_2O_3$: N, 11.96%. Found: N, 11.71%.

N,N-Diacetyl-2,6-diethyl-1,4-phenylenediamine (XIII).—The nitroamine (III) was reduced with hydrazine and palladized charcoal, giving the diamine as a colorless oil. Acetylation followed by two crystallizations from acetone–toluene afforded the bisamide as slender needles, m.p. 216–217°. Calc. for $C_{14}H_{20}N_2O_2$: N, 11.28%. Found: N, 11.30%.

4-Nitro-2,6-diethylphenol (IV).—To a cold (0–5°) solution of the nitroamine (III) (3 g.) in 50% sulphuric acid (40 ml.) was added sodium nitrite (2 g.). The mixture was left for 1 hour at room temperature and, after addition of urea to destroy excess nitrous acid, was maintained at 60° for 1 hour. During this time the phenol separated as a reddish solid. Attempted purification through the intensely yellow sodium salt was not successful but two crystallizations from methanol (Norite) afforded slightly reddish needles, m.p. 131–133° with decomposition. (Lit. m.p. 130–131° with decomposition (19).)

2,6-Diethyl-1,4-benzoquinone (V) was prepared by oxidizing the nitrophenol (IV) with lead tetraacetate, as described previously (19). It was obtained as bright yellow needles, m.p. 36–38°, by low temperature crystallization from pentane. (Lit. m.p. 35° (19); 39° (20).)

Attempts to oxidize the nitroamine (III) to the quinone, using chromic acid or lead tetraacetate, were not successful.

N-(3-Nitro-2,6-diethylphenyl)-p-toluenesulphonamide (VI).—A mixture of acetic acid (50 ml.), fuming nitric acid (4.5 ml., d. 1.5), and sulphuric acid (50 ml.) was added dropwise to a vigorously stirred suspension of the amide (I) (32 g.) in acetic acid (250 ml.) containing sulphuric acid (120 ml.). The addition required ½ hour during which time the temperature rose to 45°. After 6 hours the product was isolated by pouring the mixture onto crushed ice. Crystallization from aqueous ethanol (Norite) afforded buff prisms (17–26 g.), m.p. 149–151°. An analytical sample was obtained as pale yellow prisms after several crystallizations from benzene–hexane, m.p. 152–153°. Calc. for $C_{17}H_{20}N_2O_4S$: N, 8.04%. Found: N, 8.13%.

N-(3-Nitro-2,6-diethylphenyl)-acetamide (VIII).—Hydrolysis of the once-crystallized amide (VI) with 90% sulphuric acid gave the amine as a yellow oil. Acetylation followed by crystallization from methanol and then benzene–hexane afforded the acetamide as almost colorless needles, m.p. 153–154°. Calc. for $C_{12}H_{16}N_2O_3$: N, 11.96%. Found: N, 12.01%.

N-(3,5-Dinitro-2,6-diethylphenyl)-acetamide (VII) was commonly obtained when the acetamide (X) was nitrated in a mixture of acetic and sulphuric acids. It crystallized from toluene as pale yellow needles, m.p. 206–208° with some decomposition (capillary determination). On the hot stage, with a rapid rate of heating, the melting point was 211–212°. Calc. for $C_{12}H_{15}N_3O_5$: C, 51.24; H, 5.35; N, 14.94%. Found: C, 51.31; H, 5.31; N, 14.94%.

On a few occasions the mononitro compound (VIII) was obtained by nitrating (X) but reliable conditions for its preparation by this method were not found. Attempts to dinitrate the sulphonamide (I) were not successful, probably owing to hydrolysis.

N-(3-Bromo-2,6-diethylphenyl)-acetamide (IX) was prepared by shaking the acetamide (X) for several hours with a mixture of 98% sulphuric acid (400 ml.) and bromine (20 g.), during which time hydrogen bromide was steadily evolved. The product was isolated by pouring onto crushed ice, crystallization from benzene giving white needles (18 g.), m.p. 157–160°, raised to 161–162° by two crystallizations from methanol. Calc. for $C_{12}H_{16}NOBr$: C, 53.34; H, 5.18%. Found: C, 53.12; H, 5.95%.

N-(4-Bromo-2,6-diethylphenyl)-acetamide (XII) was obtained when the acetamide (X) was brominated in chloroform or acetic acid. It crystallized from methanol or benzene–hexane as long white needles, m.p. 181–182°. Addition of the 3-isomer (VII) depressed the melting point. Calc. for $C_{12}H_{16}NOBr$: C, 53.34; H, 5.97; N, 5.18; Br, 29.58%. Found: C, 53.30; H, 5.85; N, 5.13; Br, 30.25%.

Bromination of the sulphonamide (I) in chloroform (with or without addition of potassium carbonate), acetic acid, or sulphuric acid gave impure products having almost identical infrared spectra. Repeated crystallization from various solvents (methanol, acetone, ethyl acetate, benzene) gave white needles having melting points in the range 115–144°. Calc. for $C_{17}H_{20}NO_2SBr$: C, 53.41; H, 5.27%. Found: C, 53.58, 53.29; H, 5.25, 5.35%. Hydrolysis with 90% sulphuric acid gave, after acetylation, the 4-bromo-acetamide (XII), obtained after one crystallization from methanol.

INFRARED SPECTRA

The infrared spectra were obtained using potassium bromide disks and solutions in carbon disulphide or chloroform, and were calibrated against the spectrum of "Polystyrene".

The 1600–2000 cm.$^{-1}$ region, generally useful in orienting benzene derivatives (21, pp. 54–70), proved to be of little value as the acetamides showed strong carbonyl absorption at about 1650 cm.$^{-1}$. Comparison of the bands in the 700–1200 cm.$^{-1}$ region failed to reveal useful correlation with structure, and comparison of some of the spectra with those of the dimethyl homologues was also valueless.

ACKNOWLEDGMENTS

The authors are grateful to the Ethyl Corporation for generous samples of 2,6-diethylaniline and to Dr. B. M. Wepster for samples of certain derivatives of 2,6-dimethylaniline and for friendly correspondence. One of them (P. M. G. B.) is deeply indebted to Dr. F. A. L. Anet for his encouragement and interest.

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MICROCALORIMETRIC AND KINETIC STUDIES OF THE α-CHYMOTRYPSIN – HYDROCINNAMIC ESTER – HYDROCINNAMIC ACID SYSTEM[1]

WILLIAM J. CANADY[2] AND KEITH J. LAIDLER

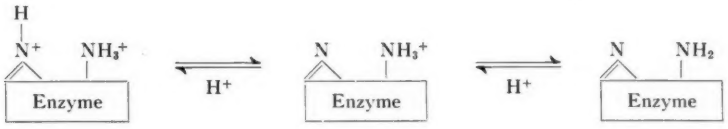
ABSTRACT

Using a microcalorimeter of the Tian–Calvet type the heat of binding of hydrocinnamic acid to α-chymotrypsin has been measured in aqueous solution over a range of pH values. The heat evolved was found to vary from about 5 to about 28 kcal per mole as the pH was varied from 5.1 to 7.8. In order to see whether these heats are due to the binding of the inhibitor at the active center of the enzyme, heats were also measured at pH 7.1 by a kinetic method, the inhibitor constant being determined over a range of temperatures; the heat calculated in this way was consistent with the microcalorimetric value. The kinetic work also gave rise to entropies of binding of the inhibitor and the substrate (methyl hydrocinnamate); these entropies are negative, the significance of which is discussed in terms of the mode of binding. It is suggested that the results are best explained on the hypothesis that the active center of the enzyme contains, in addition to the ordinary acidic and basic sites, a negatively charged group that interacts electrostatically with the anion of hydrocinnamic acid.

INTRODUCTION

A considerable amount of evidence has now accumulated regarding the nature of the active center in the enzyme chymotrypsin, and about the mechanisms of the reactions catalyzed by the enzyme. Since these matters have recently been reviewed and discussed (1) only the most important points will be referred to here. The work with DFP (2) and with other inhibitors (3, 4) has shown the enzyme to contain one active center per molecule. The pH dependence of the rate (5, 6) shows that the active center contains two ionizing groups, the active form of the enzyme being the one in which one of these groups is acidic and the other basic. A study of the kinetics of the hydrocinnamic acid hydrolysis in 20% methanol solution over a range of pH values and substrate concentrations (5) has shown that the pK's of the ionizing groups in the active center of the enzyme are 7.2 and 8.0, and that these groups are ***not*** involved in the formation of the enzyme-substrate complex but only in the subsequent steps.

The DFP work, although not entirely unequivocal, does on the whole point towards the fact (7) that the imidazole group of histidine is involved in the reaction. This group presumably corresponds to the pK value of about 7.2. The identity of the group having a pK of 8.0 (or perhaps higher, as suggested in a footnote later) is unknown, but the group might be an ω-amino group. If this is the case the ionization of the enzyme is as represented below:



As far as reaction mechanisms are concerned, it is undoubtedly the case that a Michaelis complex is formed initially. This complex appears to be formed without the participation of the ionizing groups, and the binding may involve van der Waals and other weak

[1]*Manuscript received May 30, 1958.*
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forces. By analogy with the reaction with DFP and other irreversible inhibitors, it can be concluded with reasonable certainty that the enzyme is acylated at its imidazole site during the subsequent breakdown of the complex. Evidence that this is the case has been provided by the transient-phase studies of Gutfreund and Sturtevant (8, 9).

One aspect of enzyme kinetic studies that has so far been largely neglected is that involving detailed studies of the binding of inhibitors to enzymes. A few measurements of K_i values have been made, but usually at only one pH, and few ΔH and ΔS values are known for any enzyme–inhibitor system. Such studies can provide valuable information regarding reaction mechanisms, and may indeed reveal features of the active centers of enzymes that cannot be revealed by studies with substrates. The present investigation has been carried out with the object of learning about the mode of binding of the inhibitor hydrocinnamic acid to the enzyme α-chymotrypsin, over a range of pH values. Two kinds of measurement have been made. In the first place, heats of binding of the inhibitor to the enzyme have been measured directly, using a very sensitive microcalorimeter. Secondly, partly in order to see whether the heats evolved are really due to the binding of the inhibitor at the active center of the enzyme, heats of binding were also measured by a kinetic method, the inhibitor constant being measured over a range of temperatures.

Our determinations of heats of binding by microcalorimetry are, we believe, the first in which this technique has been applied to an enzyme–substrate or enzyme–inhibitor system. The results of the measurements will be seen below to provide additional knowledge of the nature of the active center and of its interaction with substrates and inhibitors.

EXPERIMENTAL

Microcalorimetry

The microcalorimeter employed is of the conduction type of Tian (10), as modified by Calvet (11, 12), and our techniques with it have been described elsewhere (13, 14). The measurements were made at 25.0° C.

The hydrocinnamic acid was supplied by Eastman Kodak and was recrystallized from hot water; m.p. 48.5° C. A solution of hydrocinnamic acid of concentration 5×10^{-2} M in $M/15$ Sørensen's phosphate buffer (15) was used throughout all of the experiments. The enzyme used was a three-times-crystallized sample of α-chymotrypsin, supplied by the Worthington Biochemical Corporation. Immediately before each experiment a fresh chymotrypsin solution of 2×10^{-4} M was made up in Sørensen buffer of the desired pH. Ten milliliters of the enzyme solution was placed in the main calorimeter cell, and 0.5 ml of the inhibitor solution was placed in the capillary bulb. After a suitable time for temperature equilibration the capillary bulb was broken, and a small rubber bulb connected to the far end of the capillary was gently squeezed to ensure mixing. A blank was run at the same time by adding inhibitor solution to a plain buffer solution of the same pH as the buffered enzyme solution. The difference between the values obtained with the blank and the enzyme is the heat evolved by the combination of inhibitor with enzyme. The final pH of the reaction mixture was checked after the heat was measured. This value was recorded as the pH at which the heat was evolved.

Kinetics

The methyl ester of hydrocinnamic acid was prepared by refluxing the acid with an excess of methanol, a few drops of concentrated sulphuric acid being used as catalyst. The product was dissolved in ether and washed with 5% sodium bicarbonate solution

and with water. It was purified by fractional distillation, the middle 20% being collected; the boiling point was 236.5° C at atmospheric pressure. The enzyme employed was the same three-times-crystallized sample used for the calorimetric investigations. The buffer employed was the Sørensen's phosphate buffer previously used in the calorimetric determinations, but at the much lower concentration of 1.7778×10^{-4} *M*. The concentration of enzyme was approximately 1×10^{-5} *M*. The same enzyme solution was always used throughout a complete set of runs. The procedure was to measure initial reaction rates over a range of substrate and inhibitor concentrations. The range of substrate concentrations employed was 0.89×10^{-3} *M* to 2.65×10^{-3} *M*, the upper limit being imposed by the low solubility of the substrate in water. The inhibitor concentration was varied from 0.659×10^{-3} to 5.27×10^{-3} *M*. In order for the ionic strength to be maintained constant all solutions were 0.1 *M* in sodium chloride. Runs were carried out at 10.0°, 15.0°, 20.0°, 25.0°, and 30.0° C, and at a pH of 7.10.

The course of the reaction was followed by potentiometric titration, using a Radiometer Automatic Titrator as a pH meter. As the reaction proceeded small amounts of 2×10^{-2} *M* sodium hydroxide were added from a syringe micropipette in order to neutralize the hydrocinnamic acid liberated and to maintain the pH constant at 7.10. The sodium hydroxide was conveyed directly to the surface of the solution by means of a bent hypodermic needle. The reaction mixture was stirred by means of a magnetic stirrer, and the temperature maintained constant by circulation of thermostatically controlled water through an outer jacket.

RESULTS

Microcalorimetry

The heats evolved per mole are shown in Table I, and a plot of ΔH against pH is given in Fig. 1.

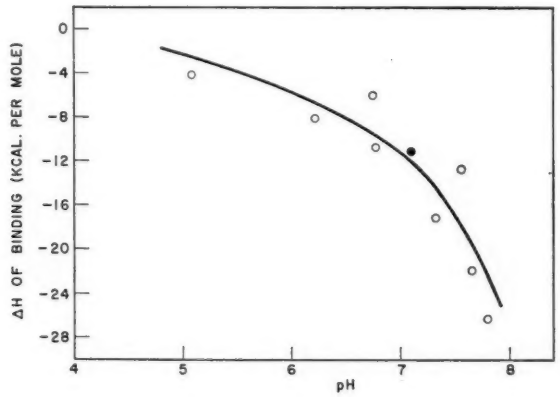

FIG. 1. Plot of ΔH of binding against pH, for the α-chromotrypsin – hydrocinnamic acid system.

Kinetics

The rates obtained at a variety of temperatures, substrate concentrations, and inhibitor concentrations are shown in Tables II and III.

TABLE I

MICROCALORIMETRIC HEATS OF BINDING FOR THE α-CHYMOTRYPSIN – HYDROCINNAMIC ACID SYSTEM

pH	ΔH (kcal per mole)
5.09	− 4.2
6.22	− 8.1
6.75	− 6.1
6.78	−10.8
7.32	−17.2
7.56	−12.8
7.65	−22.0
7.80	−26.4

TABLE II

RATES AT VARIOUS TEMPERATURES AND SUBSTRATE CONCENTRATIONS

Rates in mole liter^{-1} sec^{-1}; [S] in mole liter^{-1}

T = 10.0° C		T = 15.0° C		T = 20.0° C		T = 25.0° C		T = 30.0° C	
[S] $\times 10^3$	$v \times 10^7$	[S] $\times 10^3$	$v \times 10^7$	[S] $\times 10^3$	$v \times 10^7$	[S] $\times 10^3$	$v \times 10^7$	[S] $\times 10^3$	$v \times 10^7$
2.647	1.088	2.675	1.947	2.674	2.777	2.810	4.211	2.674	6.195
2.383	1.077	2.405	1.958	2.407	2.764	2.529	4.213	2.407	6.078
2.118	1.046	2.139	1.906	2.140	2.710	2.248	4.029	2.139	5.817
1.853	1.053	1.872	1.906	1.872	2.625	1.967	3.911	1.872	5.674
1.324	1.031	1.604	1.835	1.605	2.599	1.686	3.797	1.605	5.439
		1.337	1.787	1.337	2.485	1.405	3.699	1.337	5.101
		1.069	1.742	1.070	2.353	1.124	3.486		
				0.802	2.210	0.984	3.310		
						0.843	3.198		

TABLE III

RATES AT VARIOUS TEMPERATURES, SUBSTRATE CONCENTRATIONS, AND INHIBITOR CONCENTRATIONS

Rates in mole liter^{-1} sec^{-1}; concentrations in mole liter^{-1}

T = 10.0° C [S] = 1.337×10^{-3}		T = 15.0° C [S] = 1.337×10^{-3}		T = 20.0° C [S] = 1.604×10^{-3}		T = 25.0° C [S] = 1.405×10^{-3}		T = 25.0° C [S] = 1.967×10^{-3}		T = 25.0° C [S] = 1.124×10^{-3}		T = 30.0° C [S] = 1.324×10^{-3}	
[I] $\times 10^3$	$v \times 10^7$	[I] $\times 10^3$	$v \times 10^7$	[I] $\times 10^3$	$v \times 10^7$	[I] $\times 10^3$	$v \times 10^7$	[I] $\times 10^3$	$v \times 10^7$	[I] $\times 10^3$	$v \times 10^7$	[I] $\times 10^3$	$v \times 10^7$
0	1.004	0	1.642	0	2.136	0	4.542	0	4.834	0	3.501	0	3.272
1.315	0.830	1.318	1.397	1.318	1.907	0.659	4.159	0.659	4.554	0.659	3.238	1.319	2.819
2.629	0.721	2.637	1.169	1.637	1.653	2.637	3.170	1.319	4.222	1.319	2.803	2.637	2.486
3.944	0.633	3.955	1.042	1.955	1.506	3.956	2.739	2.637	3.811	2.637	2.455	3.956	2.293
5.259	0.570	5.274	0.902	5.274	1.312	4.615	2.681	3.956	3.444			5.274	1.959
		6.592	0.740			5.274	2.427						

Although the mechanism of the reaction is undoubtedly somewhat more complicated (8, 9) than represented by the simple Michaelis–Menten equations

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES$$

$$ES \xrightarrow{k_2} E + \text{products}$$

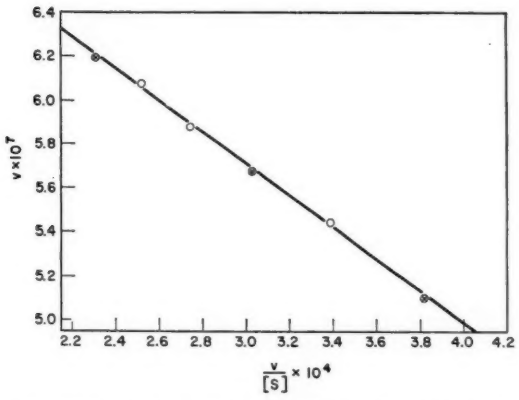

FIG. 2. Plot of v against $v/[S]$ for the hydrolysis of hydrocinnamic ester. The points with crosses represent duplicate runs.

the over-all kinetic behavior is consistent with the above mechanism; in the present treatment the above mechanism will therefore be assumed. The validity of this mechanism can be demonstrated, as first shown by Eadie (16), by plots of $v/[S]$ against v. A representative plot of this kind is shown in Fig. 2. From the slope and intercepts may be obtained the values of k_2 and $\bar{K}$; the latter is the reciprocal of the conventional Michaelis constant and is defined by

$$[1] \qquad \bar{K} = 1/K_m = k_1/(k_{-1}+k_2).$$

As referred to above there is good evidence that $k_{-1} \gg k_2$, so that $\bar{K}$ is simply the equilibrium constant for the formation of the complex.

The values of K_i were obtained from plots of v_0/v against [I]; v is the inhibited rate and v_0 the uninhibited rate. The rate equation for competitive inhibition is

$$[2] \qquad v = k_2\bar{K}[E]_0[S]/(1+\bar{K}[S]+K_i[I])$$

and from this it follows that

$$[3] \qquad v_0/v = 1+\{K_i[I]/(1+\bar{K}[S])\}.$$

The slopes of the plots were found to be proportional to $1/(1+\bar{K}[S])$; examples of such plots are shown in Fig. 3, and the lines are seen to meet the ordinate at a value of unity. The results confirm that the inhibition is indeed competitive; from the slopes, $\bar{K}$ being known, the K_i values were calculated.

Each value of $\bar{K}$ was obtained from about ten kinetic runs, every other one being made in duplicate. The values of K_i were also obtained from about ten runs. All values were calculated using the method of least squares.

Table IV shows the $\bar{K}$ and K_i values obtained in the above manner. In Fig. 4 the natural logarithms of $\bar{K}$ and of K_i are plotted against the reciprocal of the absolute temperature. The ΔH values calculated from the least-square slopes are given in Table V, together with the corresponding free energies and entropies. The second column shows the values corresponding to $\bar{K}$ and therefore related to the binding of the ester, the third column the values corresponding to K_i and related to the binding of the acid.

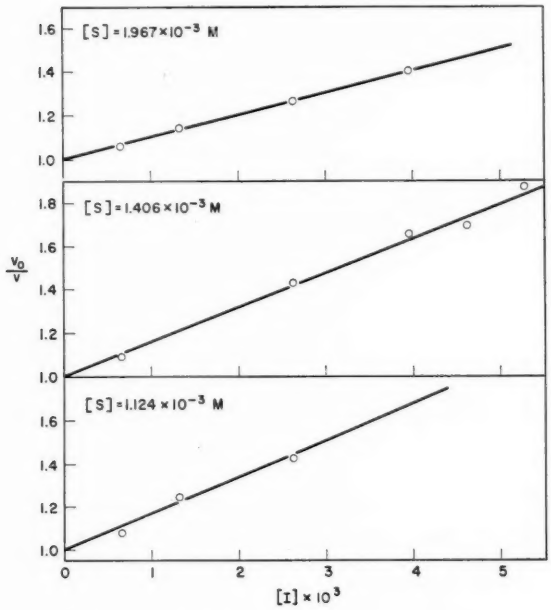

FIG. 3. Plots of v_0/v against inhibitor concentration.

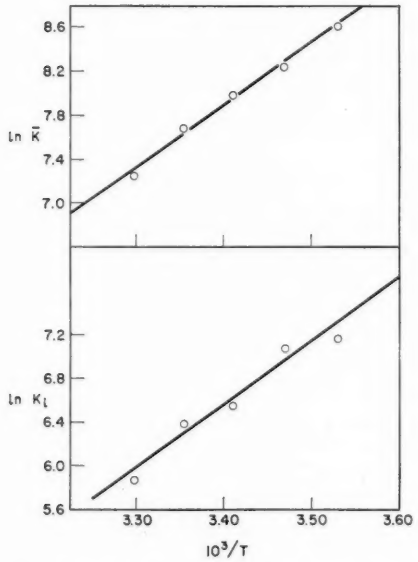

FIG. 4. Plots of the natural logarithms of $\bar{K}$ and K_i against the reciprocal of the absolute temperature.

TABLE IV

VALUES OF $\bar{K}$ AND K_i AT VARIOUS TEMPERATURES

pH = 7.10		
Temperature, ° C	$\bar{K}$ (liter mole^{-1})	K_i (liter mole^{-1})
30.0	1405	356
25.0	2170	592
20.0	2831	696
15.0	3770	1179
10.0	5488	1292

TABLE V

SUMMARY OF THERMODYNAMICAL RESULTS FOR THE BINDING OF ESTER AND ACID

pH = 7.10			
	Ester	Acid	
ΔG	− 4.55	− 3.78	kcal per mole
ΔH	−11.2	−11.0	kcal per mole
ΔS	−22.2	−24.3	e.u.

DISCUSSION

The result of greatest interest from the present standpoint is the fact that the heat corresponding to K_i, namely 11.0 kcal per mole, agrees quite closely with that obtained in the microcalorimetric studies. This is shown in Fig. 1, in which the heats are plotted against the pH; the open circles represent the calorimetric results, the closed circle the kinetic value obtained as described above. Since the microcalorimeter was being used at its very highest sensitivity there may well be an error of 10% or more in the calorimetric heats, and this largely accounts for the difference between the kinetic heat and the calorimetric ones. Additional reasons for differences are:

(1) the much higher enzyme concentration that had to be used in the calorimetric work (2×10^{-4} M as compared with 1×10^{-5} M),

(2) the fact that the kinetic work was done in 0.1 M sodium chloride solution.

In view of the similarity of the kinetic and calorimetric values there is no reason to doubt that the microcalorimetric values do correspond to the interaction between the active centers and the inhibitor. Further work to confirm this is, however, necessary, and is now being carried out at other pH values.

Other points that are worthy of comment are as follows. The close similarities between the ΔH, ΔS, and ΔG values for esters and inhibitor are consistent with the conclusions, strongly suggested by the pH studies in 20% methanol (5), that*

(*a*) $\bar{K}$ is actually an equilibrium constant,

(*b*) the binding between enzyme and substrate does not involve the ionizing groups on the enzyme.

Conclusion (*b*) suggests that the enzyme–substrate binding probably involves van der Waals forces between enzyme and substrate (1), and these forces are expected to remain practically the same if the ester is replaced by the acid.

**It should be mentioned that recent work (17, 18) indicates the pH behavior in aqueous solution to be slightly but significantly different from that in 20% methanol as used by Laidler and Barnard (5) and other workers. The pH optimum is 7.8 in 20% methanol but 8.4 in pure water. Stein and Laidler (17) are currently carrying out a detailed study of the influence of methanol on the kinetics of the reaction, with particular reference to the binding of irreversible inhibitors such as DFP, while Gill and Laidler (18) are studying the pH dependence in aqueous solution and are extending the present work on the binding of hydrocinnamic acid.*

A further insight into the nature of the inhibition is provided by a comparison of K_i at 25° C and at various pH values, as follows:

pH = 7.1	K_i = 592	Present work
pH = 7.8	K_i = 182	Neurath and Gladner (19)
pH = 7.9	K_i = 33	Huang and Niemann (20)
pH = 7.9	K_i = 33–50	Foster and Niemann (21)

Although the conditions (ionic strength, nature of buffer, etc.) are not the same in all cases, it seems clear that the inhibitor is much less strongly bound at the higher pH values.

The microcalorimetric studies have shown that the binding becomes more exothermic as the pH is raised; together with the K_i values, this implies that the ΔS of binding becomes considerably more negative with increasing pH. The ΔS of binding at pH 7.8 is in fact approximately -80, as compared with the value of -24.3 at pH 7.1.

Since the pK of hydrocinnamic acid is 4.66 (22) it is clear that the acid is almost entirely in the anionic form at all of the pH values of the present investigation. The variations in the thermodynamic quantities for the binding of the inhibitor must therefore be attributed to changes in the state of ionization of the enzyme. It is postulated that the enzyme possesses at its active center, in addition to the acidic and basic groups responsible for the actual hydrolysis of the substrate, a negatively charged group. This group must be largely neutralized at the pH of 7.1 (this follows from the close similarity of the thermodynamical values for the ester and the acid). At the values of 7.8–7.9, however, it must be assumed that this group is largely in the negatively charged form. As a result the binding of the acid anion is much less strong, and there is a large negative entropy of binding owing to the repulsion between the two charged groups.

ACKNOWLEDGMENTS

The authors are very much indebted to Dr. H. M. Papée, for very considerable help with the microcalorimetric determinations.

The work was supported by a grant from the Defence Research Board.

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THE SEPARATION OF SATURATED AND UNSATURATED FATTY ACID ESTERS BY GAS–LIQUID CHROMATOGRAPHY[1]

B. M. Craig and N. L. Murty[2]

ABSTRACT

Fatty acid methyl esters are separated according to chain length by using washed silicone grease supported on 20–40 mesh C_{22} firebrick. By using a plasticizer on the firebrick support the same esters are separated according to both chain length and degree of unsaturation. Together the two procedures can be used to determine the component fatty acids in fats and oils. Nearly parallel linear relations are obtained for saturated, monoethenoid, diethenoid, and triethenoid methyl esters when the logarithm of emergence time is plotted against the carbon number of the fatty acid.

INTRODUCTION

The development of gas–liquid partition chromatography by Martin and James (1, 2) has provided a new and powerful tool for semimicro- and micro-analyses. The rapid extension of this method to fats and oils by Martin and James (1, 2, 3), Cropper and Heywood (4, 5), Dijkstra *et al.* (6), Van de Kamer *et al.* (7), Ray (8) and the improvements developed by these workers have made possible the separation of small quantities of fatty acid esters. These separations are based on chain length and include separation of esters of odd-numbered acids and branched-chain acids. Silicone grease and Apiezon grease with or without stearic or other saturated acids have been the preferred liquid phases supported on Celite or crushed firebrick. A further development has been fractionation on the basis of unsaturation in a series of esters such as stearic, oleic, linoleic, and linolenic acids. This has been accomplished by Orr and Callen (9) and by Lipsky and co-workers (10) using commercial plasticizers as liquid phases. The first used by Orr and Callen (9) is Reoplex 400, which is a commercial plasticizer and is a polyoxyalkalene adipate. The plasticizers used by Lipsky are adipic esters of diethylene glycol and the adipic ester of diethylene glycol cross-linked with pentaerythritol.

In this laboratory gas–liquid chromatography has been used with silicone and Apiezon liquid phases for the analysis of fats and oils. Reoplex 400 was found to "bleed" extensively, particularly at temperatures over 200° C. Attempts were then made to synthesize plasticizers which would effect the separation of stearic, oleic, linoleic, and linolenic acids but which would not "bleed". A number of these have been synthesized and tested and the results are given in this paper.

EXPERIMENTAL

Silicone Column

Dow–Corning High Vacuum stopcock grease was dispersed in ethyl acetate by means of an Ultra-Turrax high speed stirrer, then precipitated out by addition of methyl alcohol and treated as described by Cropper and Heywood (4, 5). The washed silicone grease was dispersed in ethyl acetate in a round-bottom flask. C_{22} firebrick (Johns Manville) was added to the suspension (a mixture of 20–30 and 30–40 mesh 1:1 (w/w)), and the solvent evaporated at 80–90° C under vacuum in a laboratory rotary evaporator.

[1]*Manuscript received March 31, 1958.*
Contribution from the National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Saskatchewan.
Issued as N.R.C. No. 4863 and Paper No. 255 on the Uses of Plant Products.
[2]*National Research Council of Canada Postdoctorate Fellow, 1957–.*

The silicone grease was applied in a 1:4 ratio (w/w) with the crushed firebrick, and was packed in a copper column $\frac{1}{4}$ inch in diameter by 12 feet in length.

Plasticizer Columns

Two plasticizers were synthesized using a dibasic acid and diethylene glycol containing 1% by weight of diglycerol to provide cross-linking. The dibasic acids were adipic and succinic and details are given for preparation of the succinic plasticizer. A mixture of 24.0 g succinic acid, 21.2 g of diethylene glycol, 0.5 g of diglycerol, and 0.2 g of *p*-toluenesulphonic acid in a round-bottom flask was heated at 130° C/2 mm for 2 hours with occasional shaking. A clear sirupy solution resulted. The plasticizer was dissolved in ethyl acetate, washed three times with water, dried over anhydrous sodium sulphate, filtered, and the solvent removed under reduced pressure. The plasticizer was dissolved in ethyl acetate and applied to 20–40 mesh C_{22} firebrick in a 1:4 ratio (w/w) as outlined for the silicone column.

Two columns, copper tubing $\frac{1}{4}$ inch by 6 feet long, using succinic and adipic plasticizers, respectively, were coupled in series, with the succinic as the fore column. Initial tests indicated that the succinic plasticizer gave a more effective separation of the esters of stearic and oleic acids and the adipic column of the esters of linolenic and arachidic acids.

Apparatus

The gas–liquid chromatographic unit of conventional design was constructed in the laboratory. Four Gow–Mac filaments were employed with two in each of the reference and sample detectors and the bridge was operated at 150 ma. Helium was used as the carrier gas and the recorder was operated at the 2.5-mv range. The apparatus was controlled at a temperature of 210° C. The silicone column was operated at a flow rate of 100 cc per minute and the plasticizer columns at 70 cc per minute, as measured by a soap bubble unit on the outlet tube. The sample sizes varied from 3 to 15 μl, depending on the particular oil, and injection was made with a precision syringe.

The materials used in the study were the methyl esters of the fatty acids from tallow, soybean oil, lard, and herring oil, which were kindly supplied by the research laboratory of Canada Packers Limited, Toronto, Canada.

RESULTS AND DISCUSSION

Figure 1, which reproduces actual recorder charts, gives the curves that resulted for lard, tallow, soybean oil, and herring oil esters with the plasticizer column and for lard and herring oil esters with the silicone column. The position of peaks representing C_{10}, C_{12}, C_{14}, C_{16}, and C_{18} saturated acids, labelled 1, 2, 3, 4, and 5, respectively, were determined by calibration with a known synthetic mixture of these acids.

The separation of palmitic, stearic, oleic, linoleic, and linolenic methyl esters in soybean oil are comparable to those obtained by Lipsky (10) using a commercial plasticizer. The plasticizer used in the present work "bled" slightly during the first runs but little or not at all at later stages and operation of the column for a period of 3 weeks indicated no decreased efficiency. The present columns using a 1:4 ratio of liquid phase have a limited capacity, e.g. approximately 10 mg of soybean esters on 20 g of column packing before evidence of overloading is indicated.

The tallow esters on a silicone column showed C_8, C_{10}, C_{12}, C_{14}, C_{15}, C_{16}, C_{17}, and C_{18} acids as well as peaks between C_{14} and C_{15} and C_{16} and C_{17}, which may have been branched-chain acids. The tallow esters from the plasticizer column showed additional peaks which may be due to unsaturated acids of various chain lengths. Herring oil esters

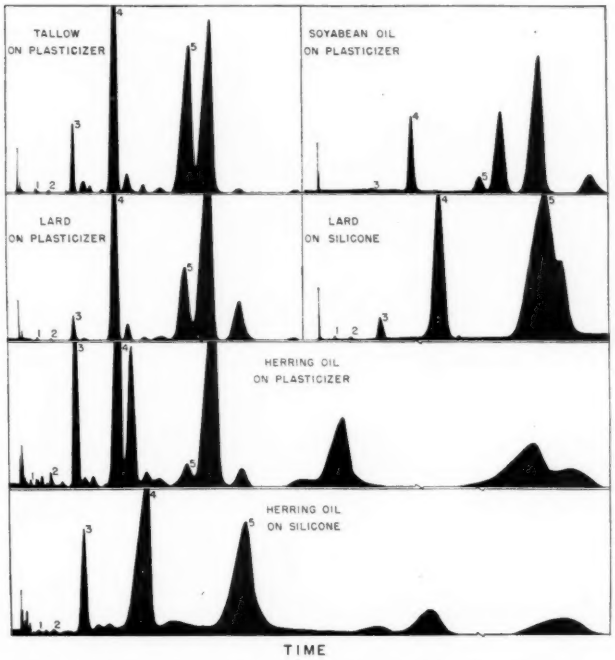

FIG. 1. Gas–liquid chromatographic separations of methyl esters of fats and oils on silicone and plasticizer columns. The numbers 1, 2, 3, 4, and 5 refer to the saturated C_{10}, C_{12}, C_{14}, C_{16}, and C_{18} acids. Peaks following these are odd-numbered or branched-chain in the case of silicone columns or unsaturated from the plasticizer column.

also showed odd-numbered fatty acids, C_9, C_{11}, C_{13}, and C_{15}, in addition to the expected even-numbered series on a silicone column. The lard esters showed even-numbered members from C_{10} to C_{20} on a silicone column and a number of unsaturated acids in each group on the plasticizer column.

Some separation of saturated and unsaturated acids took place on the silicone column within a group such as the C_{18} acids. The separation was the reverse of that accomplished by the plasticizer column in that the less unsaturated acids are retained more strongly by the liquid phase. This was proved by coupling a silicone column to a plasticizer column. The separation on the plasticizer then offset the silicone column, single peaks being obtained for each chain length. The same results were obtained with columns using Apiezon "M" as a liquid phase coupled to a plasticizer column.

The logarithm of the emergence time (time from the air peak to the sample peak) has been plotted against number of carbon atoms (Fig. 2). Peaks representing the saturated acids C_{12}, C_{14}, C_{16}, and C_{18} were plotted first and the linear relation for chain length against logarithm of retention time was established. Other peaks from various curves were plotted on the same line according to retention time only. The odd-numbered acids and compounds thought to be branched-chain acids are also represented, both from the silicone and the plasticizer columns.

The "monoethenoid" relation was made up by moving the points representing the peaks following those of palmitic, stearic, and arachidic acids, e.g. palmitoleic, oleic, and

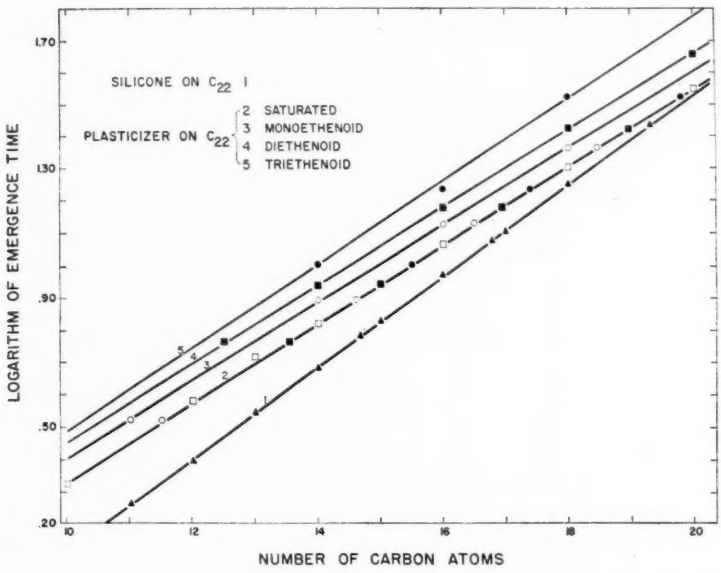

FIG. 2. Logarithm of emergence time plotted against carbon number for saturated, monoethenoid, diethenoid, and triethenoid acids from plasticizer columns and for acids from silicone column.

eicosenoic acids, to correspond to the appropriate carbon numbers. As expected, a linear relation was obtained, since the presence of one double bond would presumably have the same influence on each chain length.

The same procedure was followed for the diethenoid acids, giving a family of linear relations which are essentially parallel. The linear relation for triethenoid does not seem to be parallel to the other relations but further work needs to be done on polyethenoid acids with polyester columns to establish the slope of this line in relation to the less unsaturated acids.

Since these linear relations were established by using known esters and fatty acid esters of oils of known composition, the system is applicable for analysis of any other oil if similar conditions of temperature, flow rate, column size, and packing are used. The present system of plasticizers alone is inadequate, since the dienoic C_{16} acid has the same emergence peak as the C_{17} acid. Similarly, linolenic acid and arachidic acid examined in other oils show a simultaneous emergence. Such difficulties could be resolved by collecting the fractions from the silicone column and applying these in turn to a plasticizer column, a procedure which would require the initial separation of larger quantities of fatty acid esters.

The research on separation of saturated and unsaturated fatty acids is being continued to find liquid phases which give a more efficient separation particularly of such sequences as stearic–oleic and linolenic–arachidic acids. Preliminary results on quantitative measurements of unsaturated acids such as linoleic and linolenic which are presently done by spectrophotometric analysis indicate that the chromatographic method is equally reliable and requires considerably smaller samples.

ACKNOWLEDGMENTS

The work of Mr. T. M. Mallard, who constructed the gas–liquid chromatographic unit, and Mr. L. L. Hoffman, who aided in the analyses, is gratefully acknowledged.

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THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTRA

IV. FOUR NUCLEI: AB_3[1]

R. J. Abraham, J. A. Pople,[2] and H. J. Bernstein

ABSTRACT

The proton magnetic resonance spectrum of methyl mercaptan has been analyzed on the basis of the nuclear grouping AB_3. The spectrum calculated for $J/\nu_0\delta = 0.324$ agrees very well with that observed.

1. INTRODUCTION

This series of papers presents detailed methods of analysis of complex nuclear magnetic resonance spectra which arise when signal separations due to chemical shifts are of the same order as the spin-coupling constants. In Part I (1), the quantum mechanical methods for setting up the problem for nuclei of spin $\frac{1}{2}$ were reviewed and a notation set up for classifying groups of nuclei which gave characteristic spectra. In this paper, we shall be concerned with four nuclei of spin $\frac{1}{2}$, three of which (type B) are in equivalent chemical positions. This means that they have the same chemical shift and the same coupling constants with the fourth nucleus (type A). According to the notation of Part I, this is described as an AB_3 group if the chemical shift is of the same order as the coupling constant. It should be noted that some groups may give spectra of this type even though the B-nuclei may not be equivalent at any one instant. If the nuclei are rearranging positions rapidly (compared with the width of the spectrum in frequency units), they will become effectively equivalent, the chemical shifts and coupling constants being replaced by mean values. An important source of AB_3 spectra is likely to be methyl groups where internal rotation carries out this rapid interchange. An example of this sort is the proton spectrum of CH_3SH at 40 Mc/sec, which is analyzed in Section 3.

2. GENERAL THEORY FOR AB_3

We shall adopt the general method and notation outlined in Part I (1). This involves the construction of matrices of the Hamiltonian using a set of basic functions chosen according to the symmetry of the nuclear group. It is necessary to combine the two spin functions of the A-nucleus with the six functions for three equivalent nuclei B_3. The latter were tabulated by McConnell, McLean, and Reilly (2) and consist of four symmetrical functions

$$[2.1] \qquad (\alpha\alpha\alpha),\ (\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)/\sqrt{3},\ (\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3},\ (\beta\beta\beta)$$

and two degenerate pairs

$$[2.2] \qquad (\alpha\alpha\beta+\alpha\beta\alpha-2\beta\alpha\alpha)/\sqrt{6},\ (\alpha\alpha\beta-\alpha\beta\alpha)/\sqrt{2}$$

and

$$[2.3] \qquad (\beta\beta\alpha+\beta\alpha\beta-2\alpha\beta\beta)/\sqrt{6},\ (\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}.$$

[1]*Manuscript received June 9, 1958.*
Contribution from the Division of Pure Chemistry, National Research Council of Canada, Ottawa, Canada. Issued as N.R.C. No. 4853.
[2]*Department of Theoretical Chemistry, Cambridge, England.*

Using the group C_3, we shall call [2.1] A-functions and [2.2] and [2.3] E-functions. (The symbol A here refers to the symmetry and not to the A-nucleus.)

The next step is to construct symmetry basic functions for the complete group of four nuclei and work out the matrix of the Hamiltonian, making use of the simplifications that no mixing occurs between functions with a different total spin-component or between functions of different symmetry. Since all E-states are doubly degenerate, it is unnecessary to repeat calculations for both components, so we only consider one component of each and finally double the intensities of E-transitions. Accordingly, we shall deal only with the E basic functions $(\alpha\alpha\beta-\alpha\beta\alpha)/\sqrt{2}$ and $(\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}$.

The set of basic functions obtained by combining [2.1]–[2.3] with the functions α and β for the A-nucleus are given in Table I, together with the corresponding matrix elements of the Hamiltonian. ν_0 is the basic radio frequency employed, σ_A, σ_B, the screening constants of the two sets of nuclei, and J the A–B coupling constant. Terms involving the coupling constant between different B-nuclei are omitted, as it is known that they do not affect the observed spectrum (2). The suffix attached to each basic function gives the value of the total spin-component in the z-direction.

The determination of energies and stationary-state wave functions involves the solution of four 2×2 secular equations. We define the chemical shift δ as

$$\delta = \sigma_B - \sigma_A \tag{2.4}$$

and introduce new positive quantities D_+, D_0, D_-, D'_0 and angles θ_+, θ_0, θ_-, θ'_0 between 0 and π, such that

$$\begin{aligned}
D_+ \cos 2\theta_+ &= \tfrac{1}{2}\nu_0\delta + \tfrac{1}{2}J \\
D_+ \sin 2\theta_+ &= \sqrt{3}\,J/2 \\
D_0 \cos 2\theta_0 &= \tfrac{1}{2}\nu_0\delta \\
D_0 \sin 2\theta_0 &= J \\
D_- \cos 2\theta_- &= \tfrac{1}{2}\nu_0\delta - \tfrac{1}{2}J \\
D_- \sin 2\theta_- &= \sqrt{3}\,J/2 \\
D'_0 \cos 2\theta'_0 &= \tfrac{1}{2}\nu_0\delta \\
D'_0 \sin 2\theta'_0 &= \tfrac{1}{2}J.
\end{aligned} \tag{2.5}$$

TABLE I

BASIC FUNCTIONS AND MATRIX ELEMENTS OF THE HAMILTONIAN FOR FOUR NUCLEI AB_3

	Function $ABBB$	Diagonal matrix elements	Off-diagonal matrix elements
A_2	$\alpha\alpha\alpha\alpha$	$\nu_0(2-\frac{1}{2}\sigma_A-\frac{3}{2}\sigma_B)+\frac{3}{4}J$	
$1A_1$	$\alpha(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)/\sqrt{3}$	$\nu_0(1-\frac{1}{2}\sigma_A-\frac{1}{2}\sigma_B)+\frac{1}{4}J$	$\sqrt{3}\,J/2$
$2A_1$	$\beta\alpha\alpha\alpha$	$\nu_0(1+\frac{1}{2}\sigma_A-\frac{3}{2}\sigma_B)-\frac{3}{4}J$	
$1A_0$	$\alpha(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	$\nu_0(-\frac{1}{2}\sigma_A+\frac{1}{2}\sigma_B)-\frac{1}{4}J$	J
$2A_0$	$\beta(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)/\sqrt{3}$	$\nu_0(\frac{1}{2}\sigma_A-\frac{1}{2}\sigma_B)-\frac{1}{4}J$	
$1A_{-1}$	$\alpha\beta\beta\beta$	$\nu_0(-1-\frac{1}{2}\sigma_A+\frac{3}{2}\sigma_B)-\frac{3}{4}J$	$\sqrt{3}\,J/2$
$2A_{-1}$	$\beta(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	$\nu_0(-1+\frac{1}{2}\sigma_A+\frac{1}{2}\sigma_B)+\frac{1}{4}J$	
A_{-2}	$\beta\beta\beta\beta$	$\nu_0(-2+\frac{1}{2}\sigma_A+\frac{3}{2}\sigma_B)+\frac{3}{4}J$	
E_1	$\alpha\alpha(\alpha\beta-\beta\alpha)/\sqrt{2}$	$\nu_0(1-\frac{1}{2}\sigma_A-\frac{1}{2}\sigma_B)+\frac{1}{4}J$	
$1E_0$	$\alpha\beta(\beta\alpha-\alpha\beta)/\sqrt{2}$	$\nu_0(-\frac{1}{2}\sigma_A+\frac{1}{2}\sigma_B)-\frac{1}{4}J$	$-\frac{1}{2}J$
$2E_0$	$\beta\alpha(\alpha\beta-\beta\alpha)/\sqrt{2}$	$\nu_0(+\frac{1}{2}\sigma_A-\frac{1}{2}\sigma_B)-\frac{1}{4}J$	
E_{-1}	$\beta\beta(\beta\alpha-\alpha\beta)/\sqrt{2}$	$\nu_0(-1+\frac{1}{2}\sigma_A+\frac{1}{2}\sigma_B)+\frac{1}{4}J$	

The D-quantities are given directly by

$$[2.6]\qquad \begin{aligned} D_+ &= +\tfrac{1}{2}\{(\nu_0\delta)^2+2J(\nu_0\delta)+4J^2\}^{\frac{1}{2}} \\ D_0 &= +\tfrac{1}{2}\{(\nu_0\delta)^2+4J^2\}^{\frac{1}{2}} \\ D_- &= +\tfrac{1}{2}\{(\nu_0\delta)^2-2J(\nu_0\delta)+4J^2\}^{\frac{1}{2}} \\ D'_0 &= +\tfrac{1}{2}\{(\nu_0\delta)^2+J^2\}^{\frac{1}{2}}. \end{aligned}$$

The wave functions and energies of all states are now easily evaluated in terms of these quantities and it is possible to find the transition energies and intensities as outlined in Part I. These are given in Table II. A symbol such as $2A'_1$ is used for the state which reduces to the basic function $2A_1$ in the limit of large chemical shifts. The table is based on the assumption that $\sigma_B > \sigma_A$. If $\sigma_B < \sigma_A$ the spectrum is inverted, i.e. transition 1 is now $J+D_1$ to high field of $\gamma_0(1+\sigma_A/2-\sigma_B/2)$ instead of to low field etc.

TABLE II

TRANSITION ENERGIES AND INTENSITIES FOR FOUR NUCLEI AB_3

	Transition	Origin*	Energy (relative to $\nu_0(1-\frac{1}{2}\sigma_A-\frac{1}{2}\sigma_B)$)	Intensity
1.	$2A'_1 \rightarrow A_2$	A	$J+D_+$	$[\sqrt{3}\sin\theta_+-\cos\theta_+]^2$
2.	$2A'_0 \rightarrow 1A'_1$	A	$-\frac{1}{2}(\nu_0\delta)+D_+ +D_0$	$[-2\sin\theta_0\cos\theta_+ +\cos\theta_0\cos\theta_+ +\sqrt{3}\cos\theta_0\sin\theta_+]^2$
3.	$2E'_0 \rightarrow E_1$	A	$\frac{1}{2}J+D'_0$	$2[\cos\theta'_0-\sin\theta'_0]^2$
4.	$2A'_{-1} \rightarrow 1A'_0$	A	$-\frac{1}{2}(\nu_0\delta)+D_0+D_-$	$[2\sin\theta_0\cos\theta_- +\cos\theta_0\cos\theta_- \sqrt{3}\cos\theta_0\sin\theta_-]^2$
5.	$E_{-1} \rightarrow 1E'_0$	A	$-\frac{1}{2}J+D'_0$	$2[\cos\theta'_0+\sin\theta'_0]^2$
6.	$A_{-2} \rightarrow 1A'_{-1}$	A	$-J+D_-$	$[\cos\theta_-+\sqrt{3}\sin\theta_-]^2$
7.	$1A'_{-1} \rightarrow 1A'_0$	B	$-\frac{1}{2}(\nu_0\delta)+D_0-D_-$	$[\sqrt{3}\cos\theta_0\cos\theta_-+\sin\theta_-\cos\theta_0 +2\sin\theta_-\sin\theta_0]^2$
8.	$1E'_0 \rightarrow E_1$	B	$\frac{1}{2}J-D'_0$	$2[\cos\theta'_0+\sin\theta'_0]^2$
9.	$1A'_0 \rightarrow 1A'_1$	B	$-\frac{1}{2}(\nu_0\delta)+D_+-D_0$	$[2\cos\theta_0\cos\theta_+ +\sin\theta_0\cos\theta_+ +\sqrt{3}\sin\theta_0\sin\theta_+]^2$
10.	$1A'_1 \rightarrow A_2$	B	$J-D_+$	$[\sqrt{3}\cos\theta_+ +\sin\theta_+]^2$
11.	$2A'_0 \rightarrow 2A'_1$	B	$-\frac{1}{2}(\nu_0\delta)-D_++D_0$	$[\sqrt{3}\cos\theta_0\cos\theta_+ -\cos\theta_0\sin\theta_+ +2\sin\theta_0\sin\theta_+]^2$
12.	$2A'_{-1} \rightarrow 2A'_0$	B	$-\frac{1}{2}(\nu_0\delta)-D_0+D_-$	$[2\cos\theta_0\cos\theta_- -\sin\theta_0\cos\theta_- +\sqrt{3}\sin\theta_0\sin\theta_-]^2$
13.	$E_{-1} \rightarrow 2E'_0$	B	$-\frac{1}{2}J-D'_0$	$2[\cos\theta'_0-\sin\theta'_0]^2$
14.	$A_{-2} \rightarrow 2A'_{-1}$	B	$-J-D_-$	$[\sqrt{3}\cos\theta_- -\sin\theta_-]^2$
15.	$1A'_{-1} \rightarrow 2A'_0$	Comb.	$-\frac{1}{2}(\nu_0\delta)-D_0-D_-$	$[-\sqrt{3}\sin\theta_0\cos\theta_- -\sin\theta_0\sin\theta_- +2\cos\theta_0\sin\theta_-]^2$
16.	$1A'_0 \rightarrow 2A'_1$	Comb.	$-\frac{1}{2}(\nu_0\delta)-D_+-D_0$	$[-2\cos\theta_0\sin\theta_+ -\sin\theta_0\sin\theta_+ +\sqrt{3}\sin\theta_0\cos\theta_+]^2$

*Based on $\sigma_B > \sigma_A$.

The shape of the spectrum (apart from scale factors) is a function only of the magnitude of the dimensionless parameters $J/(\nu_0\delta)$. Some spectra calculated for a series of values of this ratio are illustrated in Fig. 1. (The labelling of transitions assumes $\sigma_B > \sigma_A$ and $J > 0$. If $J < 0$, the appearance of the spectrum is unaltered, but the transitions would have to be renumbered.) Numerical values of the transition energies are given in Table III for a series of values of $J/(\nu_0\delta)$. The scale is adjusted so that the chemical shift is one unit.

One useful feature to note is that the spin-coupling constant is given directly by the separation between lines 3 and 5.

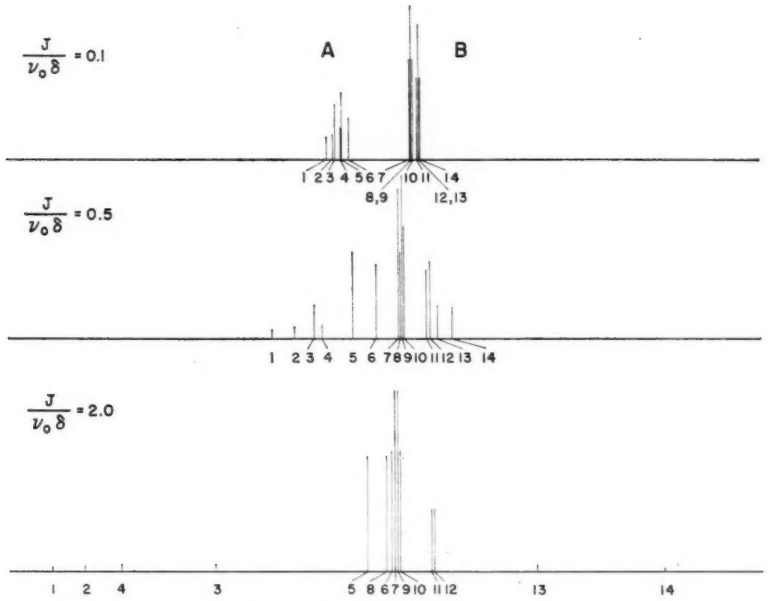

FIG. 1. Proton spectrum of CH_3SH at 40 Mc/sec. The scale is in cycles/sec and the applied field increases to the right. The frequencies are averages for several spectra to take account of drift. The numbering is that of Table II.

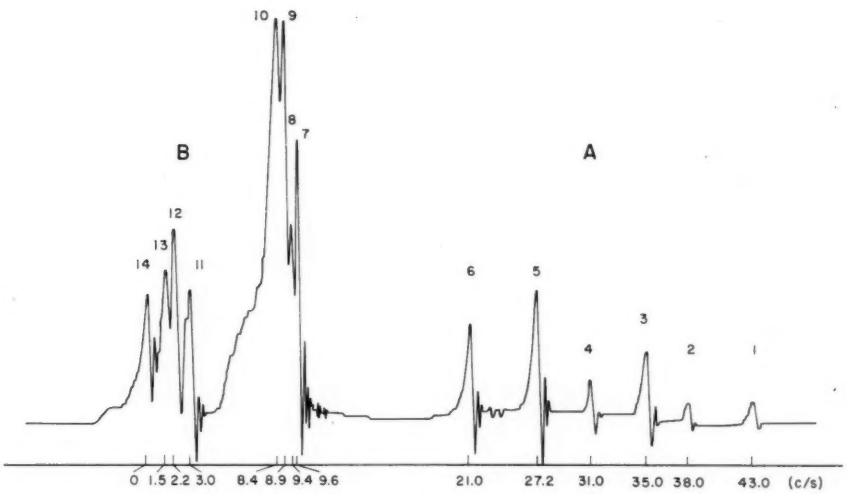

FIG. 2. Typical spectra of AB_3 group: $\sigma_B > \delta_A$ and $J > 0$. The applied field increases to the right. If $\sigma_B < \sigma_A$ the spectrum is reversed but the numbering remains the same.

TABLE III

ENERGIES OF TRANSITIONS

$J/(\nu_0\delta)$	1(A)	2(A)	3(A)	4(A)	5(A)	6(A)	7(B)	8(B)	9(B)
0	+0.500	+0.500	+0.500	+0.500	+0.500	+0.500	−0.500	−0.500	−0.500
0.1	+0.657	+0.567	+0.553	+0.468	+0.453	+0.358	−0.448	−0.453	−0.453
0.2	+0.825	+0.663	+0.620	+0.474	+0.410	+0.236	−0.397	−0.410	−0.414
0.3	+1.000	+0.783	+0.672	+0.519	+0.372	+0.136	−0.353	−0.372	−0.383
0.4	+1.181	+0.921	+0.739	+0.599	+0.339	+0.058	−0.318	−0.339	−0.359
0.5	+1.366	+1.073	+0.809	+0.707	+0.309	+0.000	−0.293	−0.309	−0.341
0.6	+1.554	+1.235	+0.883	+0.838	+0.283	−0.043	−0.276	−0.283	−0.327
0.7	+1.744	+1.404	+0.960	+0.985	+0.260	−0.076	−0.264	−0.260	−0.316
0.8	+1.936	+1.579	+1.040	+1.143	+0.240	−0.100	−0.257	−0.240	−0.308
0.9	+2.129	+1.758	+1.123	+1.311	+0.223	−0.119	−0.251	−0.223	−0.301
1.0	+2.323	+1.941	+1.207	+1.484	+0.207	−0.134	−0.248	−0.207	−0.295
1.2	+2.713	+2.313	+1.381	+1.844	+0.181	−0.156	−0.244	−0.181	−0.287
1.4	+3.106	+2.693	+1.560	+2.215	+0.160	−0.171	−0.242	−0.160	−0.281
1.6	+3.500	+3.076	+1.743	+2.594	+0.143	−0.182	−0.241	−0.143	−0.276
1.8	+3.895	+3.463	+1.930	+2.978	+0.130	−0.191	−0.241	−0.130	−0.273
2.0	+4.291	+3.853	+2.118	+3.364	+0.118	−0.197	−0.241	−0.118	−0.270

$J/(\nu_0\delta)$	10(B)	11(B)	12(B)	13(B)	14(B)	15(Comb.)	16(Comb.)
0	−0.500	−0.500	−0.500	−0.500	−0.500	−1.500	−1.500
0.1	−0.457	−0.547	−0.552	−0.553	−0.558	−1.468	−1.567
0.2	−0.425	−0.586	−0.603	−0.610	−0.636	−1.474	−1.663
0.3	−0.400	−0.617	−0.647	−0.672	−0.736	−1.519	−1.783
0.4	−0.381	−0.641	−0.682	−0.739	−0.858	−1.599	−1.921
0.5	−0.366	−0.659	−0.707	−0.809	−1.000	−1.707	−2.073
0.6	−0.354	−0.673	−0.724	−0.883	−1.157	−1.838	−2.235
0.7	−0.344	−0.684	−0.736	−0.960	−1.325	−1.985	−2.404
0.8	−0.336	−0.692	−0.743	−1.040	−1.500	−2.143	−2.579
0.9	−0.329	−0.699	−0.749	−1.123	−1.681	−2.311	−2.758
1.0	−0.323	−0.705	−0.752	−1.207	−1.866	−2.484	−2.941
1.2	−0.313	−0.713	−0.756	−1.381	−2.244	−2.844	−3.313
1.4	−0.306	−0.719	−0.758	−1.560	−2.629	−3.215	−3.693
1.6	−0.300	−0.724	−0.759	−1.743	−3.018	−3.594	−4.076
1.8	−0.295	−0.727	−0.759	−1.930	−3.409	−3.978	−4.463
2.0	−0.291	−0.730	−0.759	−2.118	−3.803	−4.364	−4.853

3. METHYL MERCAPTAN

As an example of an AB_3 spectrum we have measured the proton spectrum of CH_3SH at 40 Mc/sec. The sample of the liquid at room temperature was sealed in a spinning tube of 0.5 mm o.d. Spectra were obtained with a Varian V-4300 High Resolution Spectrometer equipped with field stabilizer. The side-band technique was used to obtain signal separations. The resonance spectrum of CH_3SH is reproduced in Fig. 2. This pattern clearly resembles the reverse of the calculated spectrum of Fig. 1 for $J/\nu_0\delta = 0.5$. The reversed spectrum corresponds to $\sigma_B < \sigma_A$ but the numbering remains the same as in Table II. The positions of the lines are easily fitted into the formulae of Table II and a good fit is obtained for

$$J = 7.85 \text{ cycles/sec}$$

[3.1] $$\nu_0(\sigma_A - \sigma_B) = 24.25 \text{ cycles/sec.}$$

Calculated transition energies and intensities using these parameters (adjusted to give agreement for line 6) are given in Table IV. The observed intensities are peak heights normalized so that the sum of the observed and theoretical intensities for the A lines are

equal and also those for the *B* lines. As expected, the agreement between observed and calculated intensities is much better for the well-resolved *A* lines than for the overlapping *B* lines.

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED SPECTRUM FOR METHYL MERCAPTAN

	Energy		Relative intensity	
Line	Calc.	Obs.	Calc.	Obs.
1	+43.7	43.0	0.40	0.49
2	+38.2	38.0	0.51	0.42
3	+34.9	35.0	1.38	1.46
4	+31.2	31.0	0.77	0.77
5	+27.0	27.2	2.62	2.78
6	+21.0	21.0	2.32	2.09
7	+ 9.9	9.6	4.31	3.54
8	+ 9.4	9.4	2.62	2.45
9	+ 9.2	8.9	5.08	5.05
10	+ 8.4	8.4	3.60	5.08
11	+ 2.9	3.0	2.40	1.71
12	+ 2.3	2.2	2.91	2.52
13	+ 1.5	1.5	1.38	1.94
14	− 0.3	0	1.68	1.66
15	−19.0		0.007	
16	−26.0		0.002	

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SECOND-ORDER UNIMOLECULAR KINETICS IN THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR[1]

W. Forst

ABSTRACT

The thermal decomposition of hydrogen peroxide vapor has been reinvestigated by the static method as a function of initial pressure at pressures up to 22 mm Hg, and in the presence of inert gas (helium, oxygen, and water) up to 100 mm Hg. In each case the apparent first-order rate constant increased linearly with pressure. It is demonstrated that under the present experimental conditions the pyrolysis of hydrogen peroxide shows behavior typical of an elementary unimolecular reaction in its low-pressure, second-order region. The reaction was accompanied by a heterogeneous decomposition which in the presence of foreign gas became inhibited. Helium was used as inhibitor over the temperature range 430–470° C, which permitted calculating the activation energy for activation with peroxide and with helium. The results can be satisfactorily accounted for by assuming a critical energy of 47–50 kcal and five effective classical oscillators for activation with peroxide and three with helium, provided deactivation occurs on every collision. Kinetic evidence against this assumption is briefly discussed.

INTRODUCTION

The thermal decomposition of hydrogen peroxide vapor has received close attention recently (1, 2, 3). The pressure dependence of the first-order rate constant observed by Giguère and Liu (1) suggested that under their experimental conditions the reaction behaved much like a unimolecular decomposition in its low-pressure, second-order region. As considerable interest attaches to such behavior, experimental verification appears worth while.

THEORETICAL

The general Lindemann mechanism for unimolecular reactions may be written in the form (4)

$$A + M \xrightarrow{a_i} A_i^* + M$$

$$A_i^* + M \xrightarrow{b_i} A + M$$

$$A_i^* \xrightarrow{c_i} \text{products},$$

where the subscript i represents energy states of A from critical energy to infinity, the asterisk denotes a molecule of reactant possessing energy in excess of the critical amount, and M represents a molecule of reactant, product, or an inert gas. To avoid needless confusion of symbols, the notation used throughout is essentially that of Johnston (ref. 4 and later papers). From the above scheme the observed (apparent) first-order rate constant is given by

$$[I] \qquad k = \frac{\text{Rate}}{[A]} = \sum_i \frac{a_i c_i [M]}{b_i [M] + c_i},$$

where square brackets indicate concentrations.

[1]*Manuscript received June 6, 1958.*

Contribution from the Department of Chemistry, Laval University, Quebec, Que. This work was supported by the Office of Scientific Research of the U.S. Air Force under Contract No. AF 18(600)-492. Based on a paper presented at the 41st Annual Conference and Exhibition of the Chemical Institute of Canada, Toronto, May 26–28, 1958.

If $b_i[M] < c_i$ for all i this expands to

[II] $$k = [M]\left\{\sum_i a_i - \sum_i \frac{a_i b_i}{c_i}[M] + \sum_i a_i\left(\frac{b_i}{c_i}\right)^2[M]^2 - \dots\right\}.$$

At the low-concentration limit

[III] $$b_i[M] \ll c_i \qquad \text{for all } i,$$

so that the second and higher terms in the bracket of [II] will be small compared with the leading term, and hence

[IV] $$k = \sum_i a_i[M] = a[M],$$

where a is the second-order constant for activation and [M] a properly weighted sum of the concentrations of reactant, product, and inert gas. Equation [IV] means that as long as the inequality [III] is satisfied, the plot of observed first-order rate constant k vs. [M] will be a straight line passing through the origin, i.e. the reaction will be second order. If the reaction is accompanied by a first-order heterogeneous reaction, there will be a finite intercept H on the k-axis, and [IV] becomes

$$k = a[M]+H.$$

If the inequality [III] is not satisfied, that is, if the pressure is not low enough, the second and higher terms in the bracket of [II] will not vanish and the plot of k vs. [M] will show a curvature.

The over-all reaction in the decomposition of hydrogen peroxide is

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2,$$

so that [IV] becomes in the presence of one inert foreign gas X

[V] $$k = a_1[H_2O_2]+a_2[H_2O]+a_3[O_2]+a_4[X].$$

Stoichiometry requires

$$[H_2O] = \tfrac{1}{2}[O_2] = [H_2O_2]_0 - [H_2O_2],$$

and it follows that

[VI] $$k = a_1[H_2O_2]_0+a_4[X]-(a_1-a_2-\tfrac{1}{2}a_3)([H_2O_2]_0-[H_2O_2]),$$

where the subscript zero refers to initial concentration. Define relative efficiency R_M of gas M with respect to reactant

$$R_M = a_M/a_1,$$

and the relative efficiency of products $\tilde{R}$

$$\tilde{R} = a_2/a_1+a_3/2a_1.$$

Substitution of $\tilde{R}$ into [VI] yields

$$k = a_1[H_2O_2]_0+a_4[X]-a_1(1-\tilde{R})\{[H_2O_2]_0-[H_2O_2]\},$$

which at zero time reduces to

[VII] $$k_0 = a_1[H_2O_2]_0+a_4[X],$$

so that [VI] can be written in the form (5)

[VIII] $$k = -\frac{1}{[H_2O_2]}\cdot\frac{d[H_2O_2]}{dt} = \frac{d\log[H_2O_2]}{dt} = k_0-a_1(1-\tilde{R})\{[H_2O_2]_0-[H_2O_2]\}.$$

This treatment makes it clear that the simple relationship implied by [IV], i.e. that at the low-concentration limit the observed first-order rate constant k is a linear function of [M], is true only for k_0. Equation [VIII] shows that $k = k_0$ only when $\bar{R} = 1$, which in general need not be the case. Hence the proper way to test experimental data for accordance with the predictions of the theory is to calculate k_0 from initial rate, or from a plot of $d \log[H_2O_2]/dt$ vs. $[H_2O_2]_0 - [H_2O_2]$.

EXPERIMENTAL

Apparatus

The apparatus was essentially the same as that described previously (1, 6). The reaction was followed manometrically, the pressure being measured by means of a transducer, and recorded by a recording potentiometer (6). A decade resistor was incorporated in the transducer input circuit to permit adjustment of input voltage. Power source was a standard 12-v automobile storage battery of 70-amp-hr capacity which gave input voltage stable to better than one part in one thousand during the course of a run if care was taken to keep the transducer at a reasonably constant temperature (78–80° C).

The reaction vessel was a 2-liter spherical Pyrex flask properly conditioned with hydrogen peroxide (6). Temperatures were measured by an electronic resistance thermometer calibrated against a certified platinum resistance thermometer; the readings refer to the temperature of the outside wall of the reaction vessel. Temperature was constant to better than 0.1° during the course of a run, and to about ±0.2° for non-consecutive runs. Hydrogen peroxide vapor was obtained by evaporating liquid 99%+ hydrogen peroxide at 75° C. As is usual in this type of work, difficulties were encountered in preparing hydrogen peroxide reservoirs free of catalytic activity. In one particular instance, when the usual treatments with hot fuming sulphuric acid and hot concentrated peroxide failed, hydrofluoric acid was tried as a last resort (7). This treatment was apparently successful, judging from the absence of oxygen streamers at 70° C under vacuum. However, this peroxide gave gas-phase decomposition rates that were clearly out of line, showing a steady daily drift toward higher values, until after a week and 50 runs they settled at 50% above the normal value. When a new peroxide reservoir, which did not receive the hydrofluoric acid treatment, was substituted, results returned to normal. The only explanation seems to be that the above treatment produced some volatile fluorosilicate capable of triggering off the gas-phase decomposition of peroxide.

Procedure for a Typical Experiment

Hydrogen peroxide was evaporated into a 5-liter mixing flask heated to 120° C, and this procedure was followed by the addition of a second gas in the required amount, the total pressure not exceeding 100 mm Hg. Five minutes was allowed for mixing, and then two consecutive runs were made on the same mixture. This procedure was followed also in the case of experiments with peroxide only. Immediately before an experiment the transducer input voltage was checked and the recorder zero adjusted. The mixture was then rapidly introduced through a scratched stopcock into the reaction vessel up to the required pressure as displayed on the recorder, the stopcock was closed, and the recorder rapidly switched to the lowest range 0–1 mv. This was necessary in order to magnify as far as possible the pressure increase accompanying the reaction, which in the presence of excess foreign gas was quite small. The time interval between introduction of one-half of the mixture (= zero time) and the actual start of the pressure–time record was about 10 seconds, so that a small extrapolation was necessary to obtain initial pressure.

The chart speeds used were generally high, i.e. such that the tracing showed small curvature, a condition that made extrapolation easier. Tracings which did not permit an unambiguous extrapolation were discarded. Initial rate was obtained by drawing a tangent to the pressure–time curve at zero time by means of a simple tangentimeter* of the type described by Latshaw (8). The decomposition was followed only long enough to obtain a pressure–time tracing convenient for evaluation.

RESULTS

The results are summarized in Figs. 1, 2, and 3; the captions are self-explanatory. Each experimental point represents the average of two consecutive runs. All straight lines were fitted to the equation

$$k_0 = m + n[\mathrm{X}]$$

by the method of least squares. Standard deviation was calculated for the slope and intercept of the straight-line portion of the peroxide plot at 431.5° C, the complete equation being

$$k_0 = (1.28 \pm 0.18) \times 10^{-3} + (23.6 \pm 1.7) \times 10^{-5}[\mathrm{H_2O_2}]_0. \qquad [\mathrm{IX}]$$

Values of the parameters m and n for foreign-gas experiments are summarized in Table I.

TABLE I

LEAST-SQUARES FIT OF FOREIGN-GAS EXPERIMENTS TO EQUATION $k_0 = m + n[\mathrm{X}]$

Temp., ° C	[X]	$m \times 10^3$ (sec^{-1})	$n \times 10^5$ (mm sec^{-1})
431.5	H_2O	2.73	17.7
431.5	O_2	2.49	3.47
431.5	He	2.45	2.52
439.6	He	4.28	3.25
448.4	He	6.82	4.25
458.4	He	8.94	6.66
468.5	He	13.2	11.0

While all of the experiments reported there were evaluated from initial rates in the manner described, three experiments on pure peroxide were performed with the object of applying equation [VIII]. The decomposition was followed to completion for 12 half-lives (~30 minutes) and the results were replotted as $\log[\mathrm{H_2O_2}]$ vs. time. As will be shown later, in this case $\bar{R} = 0.83$ so that this plot should exhibit a curvature, which two of them in fact did. The curvature was of the right order of magnitude but in opposite directions; the third run yielded a straight line for all practical purposes. It was concluded that the data were not accurate enough to sustain the test of equation [VIII], or that complications arise if the reaction is allowed to proceed too far. For this reason it was considered safer to interpret the results on the basis of initial rate measurements only. However, it seems doubtful if equation [VIII] is useful even for data of very high accuracy because the curvature of the log(concentration) vs. time plot is very slight (unless $\bar{R}$ is very much different from unity) and consequently the difficulty of estimating accurately the small difference in slope of the tangents is considerable.

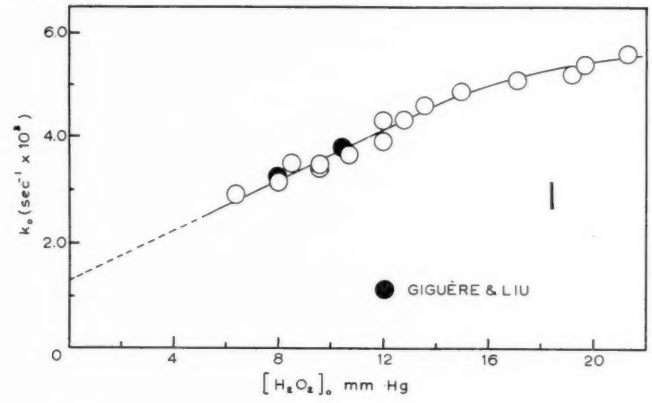
As noted previously (6), the concentration of hydrogen peroxide vapor evaporating from the liquid is subject to fluctuations, and is always less than the concentration of the

*The author is indebted to Dr. A. Sehon, of McGill University, for a loan of this instrument.

liquid itself; in addition, some decomposition occurs during the mixing time. These losses amount to about 5–10% for the two runs immediately following the mixing period, but the effect on the gas-phase decomposition rate is much less than expected, very likely because $\bar{R} = 0.83$, i.e. the collision efficiency of the products water and oxygen is quite close to the efficiency of the reactant itself. Consequently no correction was applied to hydrogen peroxide concentrations or partial pressures as determined from pressure measurements.

DISCUSSION

Basis of the interpretation of the results is equation [VII] which predicts a linear dependence of $[H_2O_2]_0$ on k_0 for $[X] = 0$, or of $[X]$ on k_0 for $[H_2O_2]_0 = \text{const}$. Inspection of Figs. 1, 2, and 3 shows that such is indeed the case for all foreign-gas experiments, and



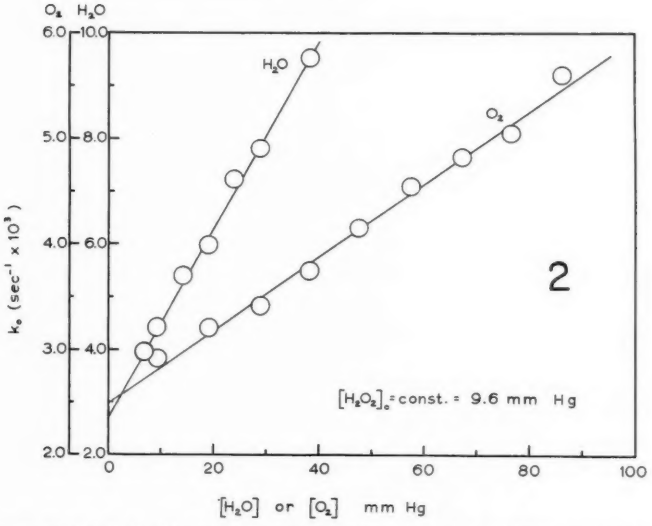


FIG. 1. Results at 431.5° C. Observed first-order rate constant k_0 plotted against initial pressure of hydrogen peroxide. Included for comparison are two points obtained by extrapolation of Giguère and Liu's results (1).

FIG. 2. Results at 431.5° C. Observed first-order rate constant k_0 plotted as a function of partial pressure of water or oxygen, with initial partial pressure of peroxide fixed at 9.6 mm Hg.

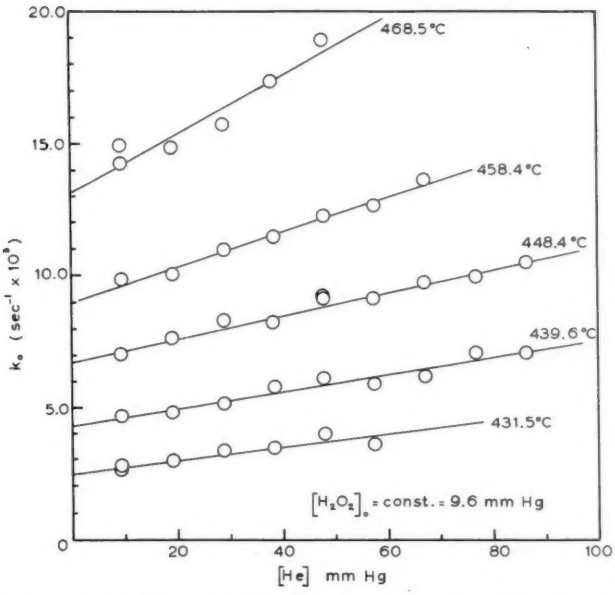


FIG. 3. Results with helium at various temperatures. Observed first-order rate constant k_0 plotted against partial pressure of helium, with initial partial pressure of peroxide fixed at 9.6 mm Hg.

for pure peroxide up to about $[H_2O_2]_0 = 15$ mm Hg. In an elementary unimolecular reaction this agreement would be sufficient proof that the reaction is in its second-order region, but the thermal decomposition of hydrogen peroxide cannot be an elementary reaction: if, as is generally conceded (1, 2), the initial step consists of a rupture of the O—O bond, it is obvious that the final products, oxygen and water, can be formed only after a more or less complex series of secondary reactions. However, by assuming a reasonable mechanism, it is easy to demonstrate that the kinetics of the gas-phase peroxide decomposition can nevertheless be simple enough to show all the essential features of an elementary unimolecular reaction.

A reasonable mechanism has been proposed by Giguère and Liu (1). It will be used here with the exception of their reaction [3]

$$2HO_2 \rightarrow H_2O_2 + O_2, \qquad [3]$$

because there is evidence, from the hydrogen–oxygen reaction, that it occurs as a first-order surface reaction (9, 10), the rate of which would be small on a clean Pyrex surface. Elimination of reaction [3] from the Giguère–Liu mechanism increases the steady-state concentration of HO_2 but has no influence on the kinetics and simplifies the algebra considerably. The reaction scheme to consider is then

$$A + M \xrightarrow{a_i} A_i^* + M$$

$$A_i^* + M \xrightarrow{b_i} A + M$$

$$A_i^* \xrightarrow{c_i} 2OH$$

$$OH+A \xrightarrow{k_2} HO_2+H_2O \qquad [2]$$

$$OH+HO_2 \xrightarrow{k_4} H_2O+O_2, \qquad [4]$$

where A represents hydrogen peroxide and the remaining symbols have their usual significance. When the usual steady-state assumption is made, the rate of disappearance of hydrogen peroxide is

$$-\frac{d[A]}{dt} = \sum_i a_i[A][M]+\sum_i \frac{a_i c_i[A][M]}{b_i[M]+c_i}-\sum_i \frac{a_i b_i[A][M]^2}{b_i[M]+c_i}.$$

If $b_i[M]<c_i$ for all i, the fractions following the summation signs may be expanded in powers of [M], and the expression for the observed first-order rate constant becomes, after some rearrangement,

$$k = -\frac{1}{[A]}\frac{d[A]}{dt} = 2[M]\left\{\sum_i a_i-\sum_i \frac{a_i b_i}{c_i}[M]+\sum_i a_i\left(\frac{b_i}{c_i}\right)^2[M]^2-\ldots\right\},$$

which is identical with [II], except for the factor 2. Consequently at the low-pressure limit

$$[IV'] \qquad k = 2\sum_i a_i[M] = 2a[M],$$

$$[VII'] \qquad k_0/2 = a_1[H_2O_2]_0+a_4[X],$$

relations analogous to [IV] and [VII]. In a similar way, it can be shown that when the pressure is high enough, $c_i \ll b_i[M]$ for all i, and

$$-\frac{d[A]}{dt} = \sum_i \frac{a_i c_i}{b_i}[A],$$

i.e. the reaction is first-order, as indeed a unimolecular reaction should be. With this demonstration the interpretation of Figs. 1, 2, and 3 in terms of equation [VII] becomes reasonably legitimate. The appearance of the factor 2 in [VII'] makes no essential difference in the arguments of this discussion.

According to equation [VII] the slopes of the straight lines in Figs. 1, 2, and 3 represent the second-order rate constant for activation; from this the relative efficiency R_M of gas M with respect to peroxide may be calculated. The results at 431.5° C are $R_{H_2O} = 0.75$, $R_{O_2} = 0.15$, $R_{He} = 0.11$. The relative efficiency of products $\bar{R}$ is then $\bar{R} = 0.75+\frac{1}{2}\times 0.15 = 0.83$, and is thus different from unity, although not sufficiently so to cause an appreciable curvature of the log(concentration) vs. time curves (see Experimental). The values for R_M reported here are comparable with efficiencies obtained in other unimolecular rate studies (11, 12), and are particularly notable for an apparent lack of correlation between the energy transfer efficiency R_M and the number of vibrational degrees of freedom (note that R_M for helium and oxygen are practically equal).

The straight line for pure peroxide (Fig. 1) does not pass through the origin; since the heterogeneous decomposition of hydrogen peroxide is known to be the first order (13), there is good reason to identify the intercept on the k-axis of the peroxide plot as representing the heterogeneous component of the reaction. On this basis, a simple calculation shows the reaction to be 65% homogeneous at 431.5° C and 10 mm Hg, compared with the estimate of 80% made by Giguère and Liu (1) for the same temperature and pressure. Presence of a heterogeneous component in the reaction requires that the inter-

cepts m in foreign-gas experiments be equal to $a_1[H_2O_2]_0+H$, i.e. there should be $m = (3.55\pm0.34)\times10^{-3}$ sec^{-1}, as determined from equation [IX] for $[H_2O_2]_0=9.6$. Comparison with the values listed in Table I for m at 431.5° C makes it at once apparent that this is not so; in fact, calculation shows that

$$m \approx a_1[H_2O_2]_0, \text{ i.e. } H \approx 0.$$

It is therefore necessary to assume that the heterogeneous reaction becomes inhibited in the presence of foreign gas, unless one is willing to make the implausible assumption that all foreign-gas experiments contain a very large systematic error in a_1 or $[H_2O_2]_0$, or both. The effective elimination of the heterogeneous reaction in foreign-gas experiments seems to be supported by the observation that reproducibility was much better in the presence of a foreign gas.

At this point it appears profitable to consider the heterogeneous decomposition of hydrogen peroxide in more detail. The sensitivity of the reaction to minute changes in surface conditions is notorious, which excludes a diffusion-controlled process. The rate-controlling process must be a reaction of absorbed species, and as such would be expected to show sensitivity to anything adsorbed on the surface, including adsorbed gases. Since adsorption of foreign gas on the surface reduces the number of surface sites available for reaction, the reaction becomes inhibited. This is apparently what happens in the case of helium, oxygen, and water. Oxygen and water are known for their inhibiting effects in other reactions (14) but a similar effect for an inert gas like helium does not seem to have been observed before. It would appear that appreciable pressures of foreign gas are needed for effective inhibition, because the amount of products (water and oxygen) formed in the course of the reaction is not sufficient for detectable self-inhibition.

If the inhibitor is strongly adsorbed, it can be shown (15) that the fractional reduction in rate of a unimolecular surface reaction is given by

$$v/v_0 = 1/K_c c_g,$$

where v = inhibited rate, v_0 = rate in absence of inhibitor, c_g = concentration of inhibitor in the gas phase, K_c = equilibrium constant for adsorption of inhibitor. For a non-localized adsorbed layer, such as would be the case with an inert gas, the expression for K_c is (16)

$$K_c = c_a/c_g = (F_a/F_g)e^{\epsilon/kT},$$

where c_a = concentration of adsorbed inhibitor, F_a, F_g = the corresponding partition functions per unit area and per unit volume, respectively, ϵ = heat of adsorption of inhibitor. Hence

$$v/v_0 = (F_g/F_a c_g)e^{-\epsilon/kT}.$$

If ϵ is small, v/v_0 will be almost temperature-independent, meaning that such inhibitor will be almost equally effective at all temperatures. The value of ϵ for helium is a few hundred calories per mole (17), which makes helium a particularly interesting inhibitor. For helium at 431.5° C,

$$H = m-a_1[H_2O_2]_0 = (0.18\pm0.16)\times10^3 \text{ sec}^{-1},$$

i.e. inhibition is very nearly complete. With a rise in temperature, v/v_0 for helium is not likely to change much; actually, inhibition is likely to become more complete, considering that temperature affects the homogeneous rate much more than the heterogeneous one owing to the difference in activation energies ($\sim$50 and 10 kcal, respectively (1)). It

seems therefore quite safe to assume that in the presence of helium $H = 0$ at temperatures above 431.5° C.

This conclusion lends a particular significance to helium experiments over a range of temperatures, as it becomes possible to obtain as a function of temperature a_1, the second-order rate constant for activation with peroxide (from the intercept m of the corresponding straight line), and a_4^{He}, the second-order rate constant for activation with helium (from slope n), and consequently also the corresponding activation energies. It would have been naturally more desirable to obtain a_1 and the corresponding activation energy more directly from peroxide experiments, but this was not possible. With rising temperature the peroxide decomposition becomes too fast to measure at higher pressures, so that the useful pressure range over which the reaction is accessible to study at higher temperatures with the present equipment is much too narrow. In addition, the effect of self-heating becomes appreciable (1).

The slopes n and intercepts m of Table I have been recalculated in terms of concentrations in moles/liter, and the results summarized in Table II. This table also includes a_1 values from oxygen and water experiments; although inhibition in these two cases does not appear quite as complete as in the case of helium, H is nevertheless roughly zero within experimental error. The data of Table II are plotted in Fig. 4 as the usual Arrhenius plot of log (rate constant) vs. reciprocal absolute temperature. The equation of each line and the standard deviation for slopes and intercepts have been calculated by the method of least squares.

The activation energy for activation with peroxide is seen to be 48.1±2.9 kcal, compared with Giguère and Liu's value of 48±3 kcal (1). Considering the wide difference

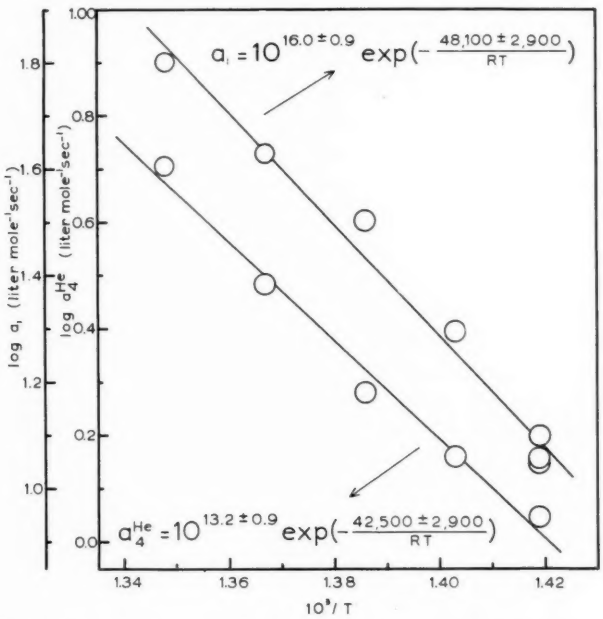


FIG. 4. Arrhenius plot for second-order rate constants for activation with peroxide (a_1) and with helium (a_4^{He}). Included is the least-squares equation of each line.

TABLE II

TEMPERATURE DEPENDENCE OF SECOND-ORDER RATE CONSTANTS FOR ACTIVATION

Temp., ° C	a_1 (liter mole^{-1} sec^{-1})	a_4^{He} (liter mole^{-1} sec^{-1})
431.5	12.5 (water)	—
431.5	11.4 (oxygen)	—
431.5	11.2 (helium)	1.11
439.6	19.8	1.44
448.4	31.9	1.91
458.4	42.4	3.04
468.5	63.3	5.08

between the two methods used for eliminating the contribution of the homogeneous reaction, this agreement is gratifying, although the closeness of the agreement is undoubtedly a coincidence. The activation energy for activation with helium is 42.5±2.9 kcal, so that, within experimental error, it equals the activation energy for activation with peroxide, as indeed in the first approximation it should because the activated state is the same in either case, namely $H_2O_2^*$. Hence for the purpose of further discussion the two equations may be written with sufficient accuracy as

[X] $$a_1 = 10^{15} \exp(-45{,}000/RT) \text{ liter mole}^{-1} \text{ sec}^{-1},$$

[XI] $$a_4^{He} = 10^{14} \exp(-45{,}000/RT) \text{ liter mole}^{-1} \text{ sec}^{-1}.$$

It will be noted that the pre-exponential factors are larger than the kinetic collision number by a factor of 10^{-3} to 10^{-4}. If the mechanism for hydrogen peroxide decomposition proposed in this discussion is accepted, it follows from equation [VII'] that the values of the rate constants a_1 and a_4^{He} given by equations [X] and [XI] should be halved. Of course this will not affect the value of the activation energy, but will make a difference of 0.3 in the power of the pre-exponential factor.

Assuming that a non-linear molecule containing N atoms may be represented by an array of $s = 3N-6$ lightly coupled classical oscillators, one obtains from statistical mechanics (18)

[XII] $$a = Z \exp(-E_c/RT \sum_{r=0}^{r=s-1} \frac{1}{r!}\left(\frac{E_c}{RT}\right)^r,$$

which for $E_c \gg sRT$ reduces to

[XIII] $$a = Z \frac{(E_c/RT)^{s-1} \exp(-E_c/RT)}{(S-1)!},$$

where Z is the kinetic collision number; the experimental activation energy E_A is related to the critical energy E_c by the equation

$$E_A = E_c-(s-3/2)RT.$$

When the values of Z and E_c are substituted in [XIII], the value of a may be adjusted to fit experimental results expressed by equations [X] or [XI] by selecting a proper value for the parameter s. The results of these calculations are given in Table III for the two extremes of the temperature range. The best fit at either temperature seems to be for helium, $s \sim 3$, $E_c \sim 47$ kcal; for peroxide, $s \sim 5$, $E_c \sim 50$ kcal. If a_1 (equation [X]) and a_4^{He} (equation [XI]) are halved, the fit is essentially the same at either temperature. Having regard to the number of normal modes in hydrogen peroxide (six), the number of effective oscillators involved seems reasonable. If E_c may be identified with the strength

of the O—O bond, and if the latter is taken as 48 kcal (1), the values found for E_c are probably as close as one could expect. These results at the same time justify the approximation $E_c \gg sRT$ involved in [XIII].

TABLE III

NUMBER OF CLASSICAL OSCILLATORS EFFECTIVE IN ACTIVATION BY PEROXIDE AND HELIUM

$T = 431.5°$ C $a_1 = 10.9$ (equation [X]) $a_4^{He} = 1.1$ (equation [XI])				$T = 468.5°$ C $a_1 = 54.3$ (equation [X]) $a_4^{He} = 5.4$ (equation [XI])			
		Calc. from [XIII]				Calc. from [XIII]	
s	E_c	a_1	a_4^{He}	s	E_c	a_1	a_4^{He}
2	45.7	0.06	0.08	2	45.8	0.49	0.64
3	47.1	0.4	0.5	3	47.3	2.9	3.8
4	48.5	1.8	2.3	4	48.8	12.4	16.1
5	49.9	6.3	8.2	5	50.3	41.9	54.5
6	51.3	19.0	24.7	6	51.8	119.7	155.4

It is well to bear in mind that equation [XII] is derived for equilibrium. When [XII] is applied to a unimolecular reaction, it is implied that

$$b_i = Z,$$

or that deactivation occurs on every collision (19, 20), a proposition which has been challenged recently (12, 21, 22). In the argument against deactivation on every collision it is tacitly assumed that the distribution function $\sum_i P_i$ defined by

[XIV] $$\sum_i P_i = \sum_i \frac{A_i^*}{A} = \sum_i \frac{a_i}{b_i}$$

has a constant value independent of the nature of foreign gas (21); it is then shown that if deactivation occurred on every collision the efficiency of a foreign gas relative to reactant would be equal to the ratio of the corresponding collision numbers. As collision numbers at a given temperature do not vary much from gas to gas, the relative efficiency of all gases should not be far from unity, a consequence which is not observed.

The weakness of this argument concerns the assumed nature of the distribution function in [XIV]. The reason why this function should not depend on the nature of foreign gas is by no means obvious; actually, it would seem reasonable to assume that $\sum_i A_i^*$ could be affected by the energy transfer efficiency of the foreign gas, and hence $\sum_i P_i$ need not be a fixed quantity for all gases. In the absence of any detailed knowledge of $\sum_i P_i$ it appears that kinetic arguments alone cannot decide whether deactivation occurs on every collision or not. As a case in point, one might take equation [XIII] where an explicit form for $\sum_i P_i$ is assumed. E_A and s are experimental quantities independent of any assumption; s is an adjustable parameter, and Z a quantity about which information is desired. Clearly, unless s is known, no information can be obtained about Z. In the absence of precise knowledge of either s or Z the problem degenerates into a case of one equation and two unknowns.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Prof. P. A. Giguère for his continued interest in this work.

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POLYOXYETHYLENEGLYCOL ETHERS. PART II*

B. A. GINGRAS AND C. H. BAYLEY

Further to the work described in Part I (1), the three ethers $C_8H_{17}O(CH_2CH_2O)_6H$, $C_{16}H_{33}O(CH_2CH_2O)_6H$, and $C_{16}H_{33}O(CH_2CH_2O)_6C_{16}H_{33}$ have been obtained from the reaction between the mono- or di-potassium salt of the hexaoxyethyleneglycol and the appropriate alkyl chloride.

The first two ethers, with terminal hydroxyl groups, are soluble in water and in the usual organic solvents. Their infrared spectra show the typical absorption of the hydroxyl at 3 μ and the broad aliphatic ether band in the 8–9 μ region. A medium band at 13.9 μ is indicative of the paraffin chain.

The last ether, lacking a hydroxyl group, behaves like a saturated hydrocarbon, being hydrophobic and soluble in organic solvents only. Its infrared spectrum is almost identical with that of the corresponding monoether except in the region of the hydroxyl absorption.

EXPERIMENTAL

n-Octylhexaoxyethyleneglycol Ether

Metallic potassium (5.9 g, 0.15 g-atom) was added in small pieces to hexaoxyethyleneglycol (42.4 g, 0.15 mole) and the mixture was stirred and heated at 130° C. After the potassium metal had reacted completely, 1-chlorooctane (25 g, 0.17 mole, b.p. 180° at 758 mm, reported in literature, 181.5° at 765 mm) (2) was added dropwise, the stirring being continued for a further 3 hours. The mixture was then cooled, diluted with acetone, and the potassium chloride was removed by filtration.

The residue was fractionally distilled under reduced pressure, and the fraction of b.p. 150°–180° at 0.1 mm (50 g) was collected. This, when distilled, gave hexaoxyethyleneglycol (b.p. 156° at 0.02 mm, 33 g) and *n*-octylhexaoxyethyleneglycol ether (b.p. 180° at 0.07 mm, 195° at 0.3 mm, n_D^{25} 1.4499, 12.7 g, 20%). The product remained yellowish even after several distillations and it was best purified by chromatography through a silica gel column. A mixture of ethyl ether and methanol, 4:1, eluted the colorless liquid in quantitative yield. Calculated for $C_{20}H_{42}O_7$: C, 60.91%; H, 10.66%. Found: C, 60.39%; H, 10.68%.

Preparation of Hexaoxyethyleneglycol Mono- and Di-hexadecyl Ethers

The reaction was carried out as above using hexaoxyethylene–glycol (25.4 g, 0.09 mole), metallic potassium (3.5 g, 0.09 g-atom), and 1-chlorohexadexane (25 g, 0.1 mole, m.p. 12°, reported in literature 12°) (3). At the end, acetone was added to the cooled mixture and the potassium chloride removed by filtration. From the filtrate separated white crystals of hexaoxyethyleneglycol dihexadecyl ether which was recrystallized from absolute alcohol to a constant m.p. 50° C (7 g, 19%). Calculated for $C_{44}H_{90}O_7$: C, 72.33; H, 12.33. Found: C, 72.33; H, 12.40.

Issued as N.R.C. No. 4835.

The residue (24 g) was chromatographed in three portions through silica gel and there was obtained from elution with ethyl ether – methanol 9:1 mixture hexadecylhexaoxyethyleneglycol ether (18.9 g, 43%), which after recrystallization from *n*-hexane had m.p. 37° C. Calculated for $C_{28}H_{58}O_7$: C, 66.40; H, 11.46. Found: C, 66.66; H, 11.58.

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RECEIVED MAY 14, 1958.
TEXTILE RESEARCH SECTION,
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SEPARATION OF CARBOHYDRATES ON COCOANUT CHARCOAL COLUMNS

F. W. BARTH AND T. E. TIMELL

Chromatographic separation on columns of charcoal–Celite has been widely used for resolving mixtures of oligosaccharides (1, 2, 3, 4, 5, 6) and methylated monosaccharides (7, 8, 9). Although Celite alone has been used for separating sugars (10), its addition to the charcoal has usually only served the purpose of increasing the rate of flow of the eluate through the columns. The commonly used mixture has been that originally suggested by Whistler and Durso (1), consisting of equal parts of Darco G-60 and Celite 535 (4, 6, 9), although "activated charcoal" (3, 11) and "animal charcoal" (8) have also been employed. Recently Jermyn (6) has advocated the use of cellulose powder instead of Celite in order to obtain faster flow. Andrews, Hough, and Powell (12) have suggested the use of very short columns, supported on a sintered plate in a Büchner funnel. This technique obviates the need for the addition of Celite, which is stated to have a tendency to contaminate the fractions obtained.

In the course of an investigation on the constitution of a polysaccharide from milkweed floss (13) it was noticed that cocoanut charcoal (a product of Fisher Scientific Co., Fair Lawn, N.J.), 50–200 mesh, pretreated with 6 *N* hydrochloric acid, water, anhydrous ethanol, and again water, was an excellent material for separating both uronic acids and methylated monosaccharides. The rate of flow, even through long columns, was very rapid. The fractions obtained were very pure and the separations were sharp. When a mixture of uronic acids, obtained on partial hydrolysis of milkweed floss (13), was added to the top of a cocoanut charcoal column (4×12 cm) and eluted with 4, 7, and 15% aqueous ethanol, respectively, three main fractions were obtained, namely a chromatographically pure aldotriouronic acid (0.20 g), 2-*O*-(4-*O*-methyl-D-glucopyranosyluronic acid)-D-xylopyranose (1.30 g) and 4-*O*-methyl-D-glucuronic acid (0.45 g), the latter in admixture with some aldobiouronic acid. Addition of a mixture of sugars obtained from the methylated, reduced, and hydrolyzed aldobiouronic acid (0.57 g) to a similar column (2×10 cm) and elution with 10 and 15% aqueous ethanol gave pure 3,4-di-*O*-methyl-D-xylose and 2,3,4-tri-*O*-methyl-D-glucose, respectively. When a mixture of galactose, glucose, and 4-*O*-methyl-D-glucose was treated similarly, elution with 1.5% ethanol yielded the neutral sugars, while the 4-*O*-methyl-D-glucose was eluted with 5% ethanol.

An acidic solution of 3-*O*-methyl-D-xylose and 2,3,4-tri-*O*-methyl-D-glucose could also be easily resolved after the acid had been removed by washing the column with water.

The adsorptive power of cocoanut charcoal appears to be somewhat greater than that of Darco G-60, as elution with larger quantities of water is necessary for complete removal of neutral sugars (14). Addition of 1–2% aqueous ethanol usually achieves the same result much more rapidly. The use of gradient elution (6, 8) would probably improve the resolution obtainable with this type of adsorbent.

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RECEIVED MAY 16, 1958.
MCGILL UNIVERSITY AND
PULP AND PAPER RESEARCH INSTITUTE OF CANADA,
MONTREAL, QUEBEC.

QUENCHING AND VIBRATIONAL-ENERGY TRANSFER OF EXCITED IODINE MOLECULES

C. ARNOT AND C. A. MCDOWELL

Recent studies (1, 6) of the quenching of the fluorescence spectrum of iodine by foreign gases have led to rather different values for the quenching efficiencies of simple molecules. Polanyi's (1) results were summarized in Table I, page 127 of Can. J. Chem., **36**, 1958, and are here reproduced.

	p, mm	I_0/I_p	I_p'/I_p	$Z_p\times10^{-8}$	$\delta\times10^{-8}$	$\delta p/Z_p$	$\epsilon\times10^{-8}$	$\epsilon p/Z_p$
H_2	9.6	3.15	0.78	2.78	0.17	0.59	0.16	0.55
D_2	8.3	3.88	0.80	1.69	(0.17)	(0.83)	(0.55)	(2.7)

$\tau = 10^{-8}$ second, I_2 pressure 0.43 mm.

The values listed above for δ, the quenching constant, were obtained from data obtained by Wood (2) for hydrogen, the same value being used for deuterium. Wood studied the fluorescence excited by sunlight and not monochromatic Hg 5461 Å, and his intensity measurements were made by a visual comparative method. The iodine pressure in Wood's experiments was 0.20 mm, as opposed to Polanyi's 0.43 mm. As neither the values of δ nor ϵ were corrected by Polanyi for the reduction of the lifetime from the "ideal mean lifetime" by self-quenching, the effect of self-quenching differs in the two experiments.

Eliashevich (3) corrected his results for self-quenching, using data obtained by Stern and Volmer (4). Assuming a value of 10^{-8} second for the "ideal mean lifetime", Eliashevich

deduced that the lifetime was reduced to 3.3×10^{-9} second at the concentration of iodine of 0.17 mm which he used. Polanyi's work can therefore be compared only with that of Eliashevich if a similar correction is made. Polanyi interpreted his results in terms of the extension of the Stern–Volmer relationship put forward by Roessler (5), which does not take into account self-quenching.

Polanyi obtained sufficient data to calculate quenching constants for hydrogen and deuterium, although for some reason he preferred to use Wood's results, which were obtained with nothing like the same precision. He states values for I_0/I_p and I_p'/I_p. The ratio of the total fluorescence intensity in the absence and in the presence of added gas (R_1), from which the quenching probability can be found, is equal to $I_0/(I_p+I_p')$.

The values of this ratio were then determined from Polanyi's data:

[1] $$R_1 = I_0/(I_p+I_p') = (I_0/I_p)/\{1+(I_p'/I_p)\}$$

Hydrogen: $I_0/I_p = 3.15$, $I_p'/I_p = 0.78$ Hence $R_1 = 3.15/1.78 = 1.77$.

Deuterium: $I_0/I_p = 3.88$, $I_p'/I_p = 0.80$ Hence $R_1 = 3.88/1.80 = 2.16$.

Polanyi's results were then interpreted in terms of the scheme put forward by Arnot and McDowell (6). Equation 24 in that paper shows:

[2] $$R_1 = (k_F+k_s[\mathrm{M}]+k_q[\mathrm{X}])/(k_F+k_s[\mathrm{M}]).$$

Rearranging,

[3] $$k_q/k_F = (R_1-1)\{1+(k_s/k_F)[\mathrm{M}]\}/[\mathrm{X}].$$

A value of 2.0×10^5 liters mole^{-1} was used for the ratio of self-quenching and fluorescence rate constants. The only other published quantitative data for self-quenching is that of Stern and Volmer (4), who found a value of 0.08 mm for the "self-quenching half pressure". On the basis of the Stern–Volmer relationship, $I_0/I = 1+\beta p$, where β is identified with k_s/k_F, this quenching half-pressure is equivalent to a value of $1/p$ for k_s/k_F, i.e. 2.25×10^5 liters mole^{-1} (1 mm Hg = 5.53×10^{-5} moles liter^{-1} at 17° C).* This value is in agreement with the value we obtained.

Substituting in equation [3]

Hydrogen: $R_1-1 = 0.77$, $k_s/k_F = 2.0\times10^5$ liters mole^{-1}, $[\mathrm{I_2}] = 0.43\times5.35\times10^{-5}$ moles liter^{-1}, $[\mathrm{M}] = 9.6\times5.35\times10^{-5}$ moles liter^{-1}

Hence $(1+k_s/k_F[\mathrm{I_2}]) = 5.60$ and $k_q/k_F = 8.4\times10^3$ liters mole^{-1}.

Deuterium: $R_1-1 = 1.16$, $(1+k_s/k_F[\mathrm{I_2}]) = 5.60$, $[D_2] = 8.3\times5.35\times10^{-5}$ moles liter^{-1}

Hence $k_q/k_F = 1.46\times10^4$ liters mole^{-1}.

Rearrangement of equation 23 in paper by Arnot and McDowell (6) yields the result

[4] $$k_T/k_F = \frac{(R_2-1)(1+[\mathrm{M}]k_s/k_F)-([\mathrm{X}]k_q/k_F)}{(1-R_3/Z)[\mathrm{X}]}.$$

Substituting for hydrogen the following values: $R_2 = 3.15$, $R_3 = 0.78$, $(1+[\mathrm{M}]k_s/k_F) = 5.60$, $k_q/k_F = 8.4\times10^3$ liters mole^{-1}, $[\mathrm{H_2}] = 9.6\times5.35\times10^{-5}$ moles liters^{-1}, $Z = 4$, we calculate

$$k_T/k_F = 1.9\times10^4 \text{ liters mole}^{-1}.$$

**Conversion factor of 1 mm = 5.35×10^{-5} moles liter^{-1} has been used here as temperature at which Polanyi's work was carried out was deduced to be ca. 27° C from his iodine pressure.*

For deuterium the following values have to be substituted in equation [4], namely: $R_2 = 3.88$, $R_3 = 0.80$, $(1+[M]k_s/k_F) = 5.60$, $k_q/k_F = 1.46\times10^4$ liters mole^{-1}, $[D_2] = 8.3\times5.35\times10^{-5}$ moles liter^{-1}. These yield the result $k_T/k_F = 2.7\times10^4$ liters mole^{-1}. The theoretical rate constants for collisions between iodine molecules and added gas molecules can be calculated from the expression:

$$[5] \qquad k = (N_0/100)\,(r_1+r_2)^2[8RT(1/M_1+1/M_2)]^{\frac{1}{2}} \text{ (liters mole}^{-1}\text{ sec}^{-1}\text{)},$$

where M_1 and M_2 are the molecular weights of the colliding species. Values of $\gamma_{I_2} = 2.7$ Å and $\gamma_{H_2} = \gamma_{D_2} = 1.1$ Å were used.

$N_0 = 6.023\times10^{23}$ molecules mole^{-1}, $R = 8.318\times10^8$ ergs/degree, $T = 300°$ K, $M_{I_2} = 254$, $M_{H_2} = 2$, $M_{D_2} = 4$, $\gamma_{I_2} = 2.7\times10^{-8}$ cm, $\gamma_{D_2} = \gamma_{H_2} = 1.1\times10^{-8}$ cm. We thus calculate

$$k_{H_2} = 4.9\times10^{11} \text{ liters mole}^{-1}\text{ sec}^{-1}$$

and

$$k_{D_2} = 3.5\times10^{11} \text{ liters mole}^{-1}\text{ sec}^{-1}.$$

On the basis of the "ideal mean lifetime" τ being 10^{-8} sec, then $k_F = 1/\tau = 10^{-8}$ sec^{-1}, and the theoretical values of k_T/k_F calculated are:

H_2 4.9×10^3 liters mole^{-1}
D_2 3.5×10^3 liters mole^{-1}.

Polanyi's experimental results interpreted this way yield values of k_T/k_F that are 3.9 times the theoretical value for H_2 and 7.7 the theoretical value for D_2 and are thus of the same order of magnitude as those found by Arnot and McDowell (6) for the quenching by other gases.

We are grateful to the National Research Council for a grant-in-aid of this research.

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Received May 26, 1958.
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The University of British Columbia,
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CHEMISCHE GESELLSCHAFT
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